WTEC Panel Report on

INTERNATIONAL ASSESSMENT OF RESEARCH AND DEVELOPMENT IN CATALYSIS BY NANOSTRUCTURED MATERIALS

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WTEC PANEL ON CATALYSIS BY NANOSTRUCTURED MATERIALS

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WTEC provides assessments of international research and development in selected technologies under awards from the National Science Foundation (NSF), the Office of Naval Research (ONR), and other agencies. Formerly part of Loyola College, WTEC is now a separate nonprofit research institute. Michael Reischman, Deputy Assistant Director for Engineering, is NSF Program Director for WTEC. Sponsors interested in international technology assessments and related studies can provide support for the program through NSF or directly through separate grants or GSA task orders to WTEC.

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The WTEC staff helps select topics, recruits expert panelists, arranges study visits to foreign laboratories, organizes workshop presentations, and finally, edits and publishes the final reports. R. D. Shelton, President, is the WTEC point of contact: telephone 410-467-9832 or email Shelton@ScienceUS.org.

WTEC Panel Report of

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FINAL REPORT

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ABSTRACT

This WTEC panel report assesses the international research and development activities in the field of catalysis by nanostructured materials. Catalysis is important for a wide variety of processes that impact manufacturing, energy conversion, and environmental protection. This study focused specifically on solid catalysts and how nanoscale structures associated with them affect their reactivity. The principal technical areas of the study are (a) design and control of synthetic nanostructures; (b) nanoscale characterization of catalysts in their working state; (c) theory and simulation; and (d) applications. The panel visited over 40 institutions and companies throughout East Asia and Western Europe to explore the active research projects in those institutions, the physical infrastructure used for the projects, the funding schemes that enable the research, and the collaborative interactions among universities, national laboratories, and corporate research centers.

A bibliometric analysis of research in catalysis by nanostructured materials published from 1996 to 2005 was conducted as part of this WTEC study. The total number of published papers as well as the expected total number of citations of those papers revealed a growing focus on this subject. Western Europe was the numerical output leader in the world; U.S. output, while published in high-impact journals, was relatively stagnant, and the number of published papers originating from China was growing exponentially and expected to exceed that from the United States in the latter half of this decade. China's rapidly expanding economy together with its growth in large-scale chemical and refining plants motivate its significant commitment to catalysis research.

The panel found that cooperation between universities and companies in catalysis R&D is common in Europe and Asia, presumably because of a more favorable intellectual property environment outside of the United States. In the area of catalyst synthesis, there is substantial activity to develop microporous materials with controlled mesoporosity and to prepare nanosized particles with preferentially exposed crystal planes. Recent advances in spectroscopy and microscopy allow the nanostructures of catalyst particles to be examined under more realistic environmental conditions approaching those of industrial reactions. Electronic structure methods and molecular simulations are now considered to be necessary tools for use alongside experiments to help guide catalysis research. The applications of much of the research observed by the panel are directly related to energy and the environment.

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We at WTEC wish to extend our gratitude and appreciation to the panelists for their valuable insights and their dedicated work in conducting this international benchmarking study of R&D in catalysis by nanostructured materials. We wish also to extend our sincere appreciation to the presenters at the North American baseline workshop and to the panel's site visit hosts for so generously and graciously sharing their time, expertise, and facilities with us. For their sponsorship of this important study, our thanks go to the National Science Foundation (NSF), the Department of Energy (DOE), the Air Force Office of Scientific Research (AFOSR), and the Defense Threat Reduction Agency (DTRA). We believe this report provides a valuable overview of ongoing R&D efforts in catalysis by nanostructured materials that can help scientists and policymakers effectively plan and coordinate future efforts in this important field.

R. D. Shelton

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FOREWORD

> We have come to know that our ability to survive and grow as a nation to a very large degree depends upon our scientific progress. Moreover, it is not enough simply to keep abreast of the rest of the world in scientific matters. We must maintain our leadership.[1]

President Harry Truman spoke those words in 1950, in the aftermath of World War II and in the midst of the Cold War. Indeed, the scientific and engineering leadership of the United States and its allies in the twentieth century played key roles in the successful outcomes of both World War II and the Cold War, sparing the world the twin horrors of fascism and totalitarian communism, and fueling the economic prosperity that followed. Today, as the United States and its allies once again find themselves at war, President Truman's words ring as true as they did a half-century ago. The goal set out in the Truman Administration of maintaining leadership in science has remained the policy of the U.S. Government to this day: Dr. John Marburger, the Director of the Office of Science and Technology (OSTP) in the Executive Office of the President made remarks to that effect during his confirmation hearings in October 2001.[2]

The United States needs metrics for measuring its success in meeting this goal of maintaining leadership in science and technology. That is one of the reasons that the National Science Foundation (NSF) and many other agencies of the U.S. Government have supported the World Technology Evaluation Center (WTEC) and its predecessor programs for the past 20 years. While other programs have attempted to measure the international competitiveness of U.S. research by comparing funding amounts, publication statistics, or patent activity, WTEC has been the most significant public domain effort in the U.S. Government to use peer review to evaluate the status of U.S. efforts in comparison to those abroad. Since 1983, WTEC has conducted over 60 such assessments in a wide variety of fields, from advanced computing, to nanoscience and technology, to biotechnology.

The results have been extremely useful to NSF and other agencies in evaluating ongoing research programs, and in setting objectives for the future. WTEC studies also have been important in establishing new lines of communication and identifying opportunities for cooperation between U.S. researchers and their colleagues abroad, thus helping to accelerate the progress of science and technology generally within the international community. WTEC is an excellent example of cooperation and coordination among the many agencies of the U.S. Government that are involved in funding research and development: almost every WTEC study has been supported by a coalition of agencies with interests related to the particular subject at hand.

As President Truman said over 50 years ago, our very survival depends upon continued leadership in science and technology. WTEC plays a key role in determining whether the United States is meeting that challenge, and in promoting that leadership.

Michael Reischman
Deputy Assistant Director for Engineering
National Science Foundation

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[1] Remarks by the President on May 10, 1950, on the occasion of the signing of the law that created the National Science Foundation. *Public Papers of the Presidents* 120:338.

[2] http://www.ostp.gov/html/01_1012.html.

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EXECUTIVE SUMMARY

Robert J. Davis

The science and technology of catalysis are important in the production of modern medicines, new fibers for clothing and construction, a wide variety of consumer products, cleaner-burning fuels, and environmental protection. The U.S. chemical industry, which relies heavily on catalysis, had record exports in 2007 and its first trade surplus since 2001. Furthermore, catalyst technologies account for over $1 trillion of revenues in the U.S. economy and about a third of its material GDP. Catalysts are considered the engines that power the world at the nanometer scale and are generally considered to be the most successful application of nanotechnology. For these reasons, the World Technology Evaluation Center initiated a study in 2006 to assess the research and development activities related to catalysis by nanostructured materials under the sponsorship of the National Science Foundation (NSF), the Department of Energy (DOE), the Air Force Office of Scientific Research (AFOSR) and the Defense Threat Reduction Agency (DTRA). The information from the assessment will be used to identify high-impact research areas worth exploring in U.S. R&D programs, clarify research opportunities and needs for promoting progress in the field, identify opportunities and mechanisms for international collaboration, and evaluate the position of foreign research programs relative to those in the United States. The principal technical focus areas of the study were

- design and control of synthetic catalytic structures
- nanoscale characterization of catalysts in their working state
- theory and simulation
- applications

WTEC recruited a panel of eight U.S. experts in the field to perform the assessment. Although a worldwide assessment of this kind normally begins with a benchmarking exercise to establish the state-of-the-art in U.S. R&D programs, a report from the 2003 U.S. National Science Foundation workshop "Future Directions in Catalysis: Structures that Function at the Nanoscale" (NSF 2003) served as the reference point for U.S. activities in the focus area of the study. Therefore, the current project was performed in the following four phases:

1. *Conduct a bibliometric analysis to establish world trends in publishing*. The analysis examined publication trends by various countries over the last decade. Results were used to confirm and identify new sites selected by the panelists to visit.
2. *Visit a number of the world's leading university, government, and industry laboratories*. The WTEC panelists visited 20 sites in China, Japan, and the Republic of Korea during June of 2007 and 22 sites in Europe in September of 2007.
3. *Report findings in a public workshop*. The panelists reported their findings to the U.S. sponsors, the catalysis community and the general public at a workshop held at the FDIC L. William Seidman Center in Arlington, VA, on November 29, 2007. The workshop, entitled "Assessment of International R&D in Catalysis by Nanostructured Materials," was a public forum in which panelists presented overall findings, specific examples from the site visits, and general conclusions. The workshop also allowed for discussion and critical review of the findings.
4. *Compile the findings into a written report*. This document represents the written record of the study that will be made available to the sponsors, funding agencies, policymakers, the catalysis community, and the general public. This report is available on the Web at http://www.wtec.org/catalysis/.

PRINCIPAL FINDINGS

Bibliometric Analysis of Catalysis Papers

Several important quantitative outputs were determined by the bibliometric analysis (see full analysis in Appendix B). First, catalysis papers in the decade of the study, 1996–2005, represented about 1/60th of the world science output, and the growth rate in catalysis papers (5.4%) exceeded that of all science papers (2.9%), indicating a growing importance of catalysis research in the world. The output of catalysis papers by 13 Western European countries exceeded the total produced by the United States by almost a factor of two. Moreover, there was a significant growth in the number of papers from the People's Republic of China from 1996–2005, while the number of papers from the United States over the same time period was essentially stagnant. In 1996, the catalysis papers from the United States outnumbered those from China by a factor of 6; however, the large disparity between China and the United States was largely eliminated by 2005, and reasonable extrapolation of the exponential growth of Chinese output suggests that the United States now lags China in the number of catalysis papers.

A second quantitative aspect of the bibliometric analysis involved a country's relative commitment (RC) to catalysis. The RC measures the importance of catalysis research within a particular country, with the RC value for the entire world being unity. The very high relative commitment of China (RC >2) to catalysis research over the decade of the WTEC bibliometric study is consistent with its exponential growth in published papers and contrasts with a very low commitment of the United States to catalysis research (RC ~0.6). The relative commitment of Western Europe to catalysis varies by country, but is generally near the world average (RC = 1).

In terms of qualitative comparisons, the papers published by U.S. researchers appear in journals with the highest potential impact, whereas the papers published in East Asia appear in journals with below average impact factors. The countries of Western Europe publish in journals with impact factors near the world average for the field. Since the Western European countries publish a high volume of papers, the total impact from Western Europe dominated the world over the decade of the WTEC bibliometric study, and the gap between Western Europe and the United States widened over that decade.

The results of the WTEC bibliometric analysis suggest that the United States had a significant, but not dominant, position in catalysis research over the decade 1996–2005. Western Europe led the world in both total number of papers published and the total citation impact. However, the very high relative commitment of East Asia to catalysis research, particularly in China, has fueled an exponential growth in the number of published papers in the last decade and will soon challenge the position of both the United States and Western Europe.

Financial Support of Catalysis Research

The financial models used to support catalysis research vary widely around the world. As a baseline for comparison, the U.S. National Science Foundation and Department of Energy support catalysis research at universities at a level of approximately $30 million per year, with nearly half of that originating from the Basic Energy Sciences program at DOE. The Catalysis and Biocatalysis Program at NSF, together with contributions to special programs such as Nanoscale Interdisciplinary Research Teams (NIRT), Nanoscale Exploratory Research (NER), and Partnerships for International Research and Education (PIRE), contribute approximately $7 million per year to U.S. university research. The total support from the DOE Office of Science, the DOE Technology Offices, other governmental agencies, and U.S. business for catalysis research at the U.S. national laboratories is estimated to be about $45 million. Although catalysis research is also funded by other agencies of the U.S. government such as the Department of Defense and by the private sector through corporate contracts, the major research activities in fundamental catalysis are supported by NSF and DOE.

The different financial models used throughout the world all appear to be effective at supporting catalysis research, and no single system can be declared as the best. However, certain aspects of each deserve close

examination for possible adoption in the United States. For example, the sustained level of baseline funding provided to a science-oriented institution such as the Fritz Haber Institute (FHI; see site report in Appendix D) allows for effective utilization of a highly trained research staff that is necessary to build the world's next-generation scientific instruments. However, a stable funding stream is not the only unique feature that allows the institution to function at a very high level scientifically. Justification of research directions at the FHI is based on recommendations from an external evaluation committee of scientific experts from around the world instead of on classical numerical outputs such as papers and patents. The stable source of funding for long-term research goals at the FHI contrasts with the typical three-year granting cycle at the U.S. government agencies, which also require yearly justifications for grant expenditures. This difference in funding strategy between the U.S. government and the FHI was highlighted during the WTEC visit as a major reason why certain kinds of research and instrument development are unique to the FHI.

The consortia model developed within and throughout the European countries is another strategy for funding research. These consortia tend to be most effective within a single country, presumably because of the ease of communication, shared cultural identity, and geographic proximity of participating institutions. Although pan-European initiatives have also experienced success, a significant fraction of funding in those initiatives is dedicated to travel and collaboration instead of directly supporting research.

European and Asian countries have done an excellent job combining academic research with national laboratory activities. The combination is almost seamless at many institutions, with principal investigators, professors, doctoral students, and research staff members working together on common goals. There appears to be a more significant separation between academic catalysis research in the United States and its complement at the mission-oriented DOE national laboratories.

Support of doctoral students and postdoctoral researchers on U.S. research grants tends to consume the major fraction of direct charges. In countries like China and Korea, government programs that fund students directly for their graduate education in areas of national importance remove the need to fund students directly on research grants. Although it is unclear whether or not that system is superior to funding students directly on grants, it does appear to be similar to the graduate training grant programs in the United States that are common in other fields.

WTEC panelists found significant industrial collaborations at most of the sites and had the impression that industrial support was more prevalent outside of the United States. The reasons appear to be many, such as a lower cost of performing research outside of the United States, a more cooperative intellectual property environment outside of the United States, and possible access to emerging world markets for the next users of catalytic technologies. Moreover, the panel noted in its visits overseas the high quality of pilot plant facilities and catalytic reactor systems capable of industrial operating conditions located within academic settings. The infrastructure for fundamental research on catalyst synthesis and characterization combined with industrially-relevant catalyst testing appeared to exceed that of typical academic catalysis laboratories in the United States.

Routine equipment for catalysis research such gas chromatographs, reactors, vacuum chambers, adsorption systems, and bench-top spectrometers, as well as major research instruments such as electron microscopes, nuclear magnetic resonance spectrometers, and X-ray diffractometers, are generally available in labs worldwide. In addition, researchers appear to have ready access to synchrotron light sources for advanced *in situ* characterization of catalysts. However, the WTEC panelists reported a significant concern with the aging U.S. catalysis infrastructure compared to that observed in East Asia and Europe. The difficulties U.S. researchers currently encounter with acquisition of new instruments routinely used for catalysis research could severely impact U.S. competitiveness in the very near future.

GENERAL OBSERVATIONS

Catalysis is often associated with large-scale chemical, petrochemical, or oil refinery processes, which are areas of rapid growth in Asia but are fairly stagnant areas in the United States and the European Union. Although Asia's rapidly expanding economy accounts for its major growth in catalysis research, the reasons

for the dominant position of Western Europe in catalysis research output are not so straightforward. Several key factors are likely to contribute to this result. First, catalysis is generally viewed outside of the United States as a fundamental science that enables discovery and development of technology in a variety of energy- and chemicals-related fields. Therefore, catalysis research is pursued in chemistry and physics departments throughout Europe, with much smaller levels of activity in European chemical engineering departments. Within the United States, heterogeneous catalysis has been viewed as a mature field that is studied mainly in chemical engineering departments. Chemistry departments in the United States tend to support much more fundamental studies involving model surfaces in pristine environments, homogeneous or single-site molecular catalysis, and biocatalysis. This artificial division allowed heterogeneous catalysis in the United States to be incorrectly perceived as an applied field of research instead of one with the potential for fundamental discovery.

Another reason European catalysis appears to have a dominant position is the close coupling of universities and national laboratories with industry. Companies within several of the countries the WTEC panel visited appear to campaign for catalysis research at the national level. This kind of advocacy support from companies, together with research contracts involving universities and government labs, indicates a significant role of the private sector in setting research directions.

Moreover, the current intellectual property (IP) environment in Europe appears to foster university-company relations, at least more so than in the United States. However, there are indications that European universities are beginning to explore the position of many U.S. universities on IP ownership and may soon move in the direction of the United States.

Finally, the overall level of investment in catalysis research in Europe simply appears to be higher than that in the United States. Although the United States is starting to see large block grants from companies such as BP and the Dow Chemical for catalysis research at universities, the combined investment of the U.S. government (mainly NSF and DOE) and the industrial sector in university and national laboratory research appears to be far below that of the European countries.

The WTEC panelists observed the use of high-throughput instrumentation in both Asia and Europe. For example, robotic synthesis of zeolite materials and high-throughput reaction testing allowed for discovery of new catalytic materials with unique properties at the Instituto de Tecnología Química (ITQ) in Valencia, Spain (see site report, Appendix D). Also, the Center for Microchemical Process Systems at KAIST (Korea Advanced Institute of Science and Technology) makes extensive use of high-throughput screening methods for discovery of new materials. New instrumentation recently purchased at institutions throughout Asia and Europe was aimed at rapid analysis of catalyst samples. Since research abroad is often carried out in major centers of activity, some of the instrumentation was actually invented and constructed in-house. This model contrasts the operation of most U.S. academic laboratories, which have neither in-house expertise for tool creation nor the resources for tool construction.

The WTEC panel also noted the effective use of permanent research staff positions in laboratories outside of the United States. In the vast majority of sites visited, including those associated with institutes and universities, the number of dedicated staff members in support of the research activities appeared to far exceed those associated with U.S. laboratories. The employment of highly skilled technical staff members at the Fritz Haber Institute was highlighted during the WTEC visit as a major reason why next-generation research instruments can be designed and built within the facility. The instruments were far too complex to be constructed solely by graduate students and short-term postdoctoral researchers. The U.S. current funding models do not support the same level of technicians, and academic institutions do not appear to have funds available for additional positions; in fact, many U.S. researchers are experiencing a decrease in technical staff at their universities.

TECHNICAL THEMES OF THE STUDY

The chapters in this report present the findings of the panel on the technical themes of the study: synthesis, *in situ* characterization, theory and simulation, and applications. Regarding catalyst synthesis, several

countries were actively pursuing new methods to produce highly structured solids such as zeolites and carbons having both micropores and mesopores. Moreover, preparation and stabilization of metal and metal oxide nanoparticles with controlled facets, sizes, and compositions are also areas of wide interest. Characterization of nanostructured catalysts by environmental electron microscopy is revealing how nanoscopic features are affected by the surrounding environment; this advanced method of observation will be pursued more aggressively with the increasing availability of commercial instruments. *In situ* spectroscopy has now become a routine method for catalyst characterization around the world. However, rapid improvements in temporal and spatial resolution of many spectroscopic methods, as well as adaptation of methods to allow for interrogation of catalysts under industrial reaction conditions, are enabling collection of an unprecedented level of new information on the structure of catalysts in their working state. Theory and modeling have gained universal acceptance as necessary tools for advancing catalysis science. Improvements in method accuracy, computational speed, and model development have moved theory to a position alongside experimentation in many laboratories. Theory has excelled in the prediction of atomic structure and spectroscopic features of catalytic materials. Although the prediction of reaction kinetics is still developing, theory is being used to suggest novel compositions to improve catalytic performance.

The key applications stimulating most of the catalysis research worldwide were related to energy and the environment. Conversion of nonpetroleum feedstocks such as coal, natural gas, and biomass to energy and chemicals was a high priority in nearly all of the countries the WTEC panel visited. China, in particular, has a major emphasis on energy applications, especially those involving the conversion of coal to liquid fuels. Significant activities in photocatalysis, hydrogen generation, and fuel cells are being carried out in many locations. There is a general recognition that energy carriers and chemicals should be produced, and ultimately used, with as little impact on the environment as possible; catalytic solutions are thus being pursued in this framework of environmental sustainability. Catalytic production of ultra-low sulfur fuels, use of renewable carbon sources and sunlight, conversion of the greenhouse gas CO_2 to useful products, highly selective oxidation of hydrocarbons, and catalytic after-treatment of waste streams are all being pursued vigorously around the globe. A growing area of interest is the catalytic transformation of various plant sources to energy-relevant compounds such as bio-oil (a carbonaceous liquid that can be blended into a refinery stream), biodiesel fuel, hydrogen, alcohols, etc. However, the targeted plant feedstocks depend on the native vegetation within a particular country.

CONCLUSIONS

Catalysis by nanostructured materials is an active area of research around the globe, and its rate of growth appears to be increasing faster than that of all science, presumably because of significant concerns regarding future energy security and environmental sustainability. Western Europe appears to hold the dominant position in the world in terms of research paper output, but the rapid growth of research in Asia could challenge that position in the near future. The overall investment levels in catalysis research in Western Europe and Asia appear to be significantly greater than that in the United States. Because 1996–2005 U.S. publications were the highest cited in the world, research funds in the United States are apparently distributed effectively to the highest-quality laboratories. The overall impact of U.S. research, however, is dampened by a much smaller output relative to Western Europe and an overall growing output from Asia. The technical themes involving catalyst synthesis, characterization, theories, and applications, have specific components that are similar to those in U.S. research programs, but the level of research activity in particular areas often depend on regional needs.

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CHAPTER 1

OVERVIEW OF CATALYSIS BY NANOSTRUCTURED MATERIALS

Robert J. Davis

INTRODUCTION TO THE STUDY

The science and technology of catalysis have played a critical role in improving our standard of living over the last century. Materials produced by catalytic technology are responsible for modern medicines, new fibers for clothing and construction, a wide variety of consumer products, cleaner-burning fuels, and environmental protection. The catalytic process used to produce high octane aviation fuel helped secure the victory of the Royal Air Force in the Battle of Britain during World War II. More recently, the widespread use of automotive catalytic converters is responsible for cleaning auto exhaust gases and improving air quality in cities around the world. The overall economic impact of catalysis cannot be overemphasized. For example, the U.S. chemical industry, which relies heavily on catalysis, had record exports in 2007 and its first trade surplus since 2001 (Shelley 2008). Furthermore, catalyst technologies account for over $1 trillion of revenues in the U.S. economy and about a third of the material GDP (Davis and Tilley 2003).

Fundamental discoveries in catalysis have been recognized many times over the previous 100 years. The Nobel Prize (see http://nobelprize.org/) was awarded to Sabatier (1912) and Langmuir (1932) for their pioneering research on catalytic hydrogenation and oxidation reactions on metals, respectively, and Ziegler and Natta received the Nobel Prize in 1963 for their novel catalytic process to make plastics and fibers. Altman and Cech were recognized with the same honor in 1989 for their discovery of catalytic properties of RNA, while Knowles, Noyori, and Sharpless shared the Nobel Prize in 2001 for their research on chiral catalysis. Most recently, the 2007 Nobel Prize was awarded to Gerhard Ertl for his elucidation of catalytic processes on solid surfaces.

The science and technology of catalysis is more important today than at any other time in our history. Since extraction of the earth's fossil fuel resources will reach peak production in the coming century, the cost of energy and chemicals from hydrocarbon resources will continue to increase in the near future. Also, the general consensus that global climate change can be influenced by human activities has motivated researchers to find new manufacturing processes that are environmentally sustainable. Catalysis will certainly play a central role in the development of new energy sources and environmentally benign chemical technologies.

A catalyst by definition is a substance that facilitates the transformation of reactants to products through a repeated cycle of elementary steps in which the last step regenerates the catalyst to its original form (NRC 1992). If a catalyst is present in the same phase as the reactants and products, it is called homogeneous, whereas if the catalyst is in a different phase, it is called heterogeneous. One example of a heterogeneous catalyst is found in the automotive catalytic converter and is composed of nanometer-size transition metal particles supported on a solid carrier. In that case, combustion gases first adsorb on the transition metal particles and then react to form relatively harmless products that desorb into the exhaust stream. Many

industrially relevant catalysts are heterogeneous, or solid-phase, which allows for very large scale continuous operation at elevated temperatures and pressures.

Since heterogeneous catalysis is a molecular event occurring at a solid-fluid interface, the nanostructure surrounding the reactive interface, known as the active site, can significantly influence the observed rate of reaction (referred to as catalytic activity) and the distribution of observed products (known as selectivity). Electron micrographs of a supported transition metal catalyst are shown in Figure 1.1. The nanometer-size particles of rhodium metal are the active catalytic component, and the silica provides a high-surface-area medium to disperse the metal particles. The nature of the exposed rhodium crystal planes as well as the presence of corners, edges, and defects on the metal particles can influence the activity and selectivity of a particular reaction on the catalyst. In addition to the exposed metal atoms, the nanoscopic environment around heterogeneous catalysts can be affected by many other parameters, such as the bulk crystal structure, composition of the support, addition of a promoter, effect of micropores, polarity of the reaction medium, chirality of ligands, and nearby presence of another "active site." In essence, catalysis by nanostructured materials is a multidimensional phenomenon. Because catalysts orchestrate chemical reactions in a highly controlled spatial and temporal manner, they are considered the engines that power the world at the nanometer length scale (Davis and Tilley 2003). Indeed, catalysts are undoubtedly "the most successful current application of nanotechnology" (Davis and Tilley 2003).

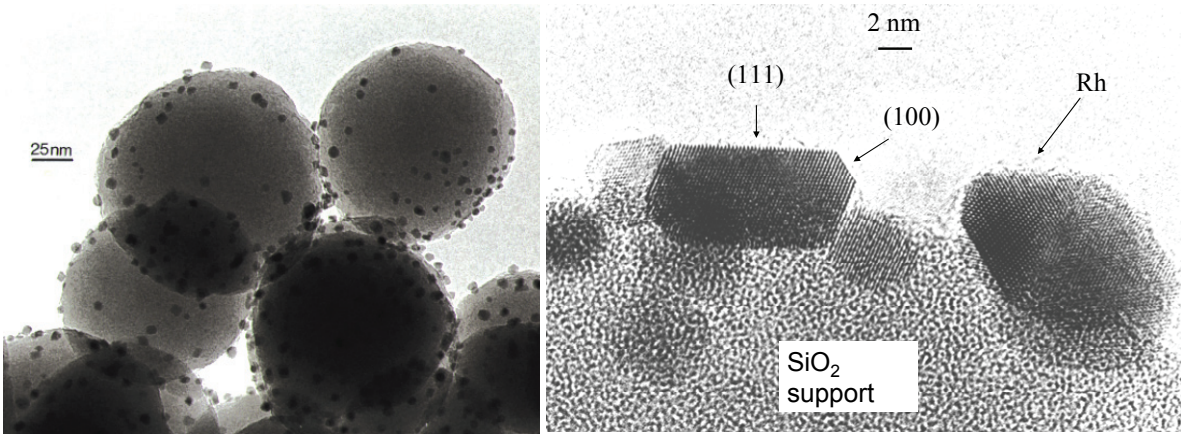

Figure 1.1. Rhodium metal particles supported on silica carrier (left). The high-resolution electron micrograph (right) shows how small supported Rh crystallites expose low index faces (left photo courtesy of Abhaya Datye; right photo from Datye 2000, © Kluwer Academic).

On June 19th and 20th, 2003, a U.S. National Science Foundation (NSF) workshop, "Future Directions in Catalysis: Structures that Function at the Nanoscale," was held at NSF headquarters in Arlington, VA (Davis and Tilley 2003). The organizers, Professor Mark Davis (California Institute of Technology) and Professor Don Tilley (University of California, Berkeley), assembled a distinguished group of 34 participants, primarily from U.S. academic institutions, government agencies, national laboratories, and major companies, to assess the state-of-the-art in the field and to provide visionary statements on the future directions of catalysis research. The workshop was organized around three working groups focused on (1) synthesis, (2) characterization, and (3) theoretical modeling of catalysts; these topics formed the basic framework of the current study.

Although the recommendations from the NSF workshop are too lengthy to reproduce here, several key concepts influenced the organization of the current international assessment. First, synthesis of new nanoscopic catalysts will require fundamental understanding of molecular-scale self-assembly and complex, multicomponent, metastable systems. The new tools of nanotechnology will likely play a key role in the synthesis of new catalytic structures. A second finding of the workshop is that new *in situ* characterization methods that extend the limits of temperature, pressure, and spatial resolution are needed to probe nanostructured catalysts in their working state. Finally, significant advances in theoretical descriptions of complex reactions and in models that span multiple time scales are required to improve the predictive

capabilities of computation, especially in liquid phase systems. A grand challenge that emerged from the workshop is "to control the composition and structure of catalytic materials over length scales from 1 nanometer to 1 micron to provide catalytic materials that accurately and efficiently control reaction pathways" (Davis and Tilley 2003).

Following the 2003 NSF workshop, four U.S. government sponsors asked the World Technology Evaluation Center (WTEC) to organize a study to assess the worldwide state of the art and research trends in catalysis by nanostructured materials. The National Science Foundation, the Department of Energy (DOE), the Air Force Office of Scientific Research (AFOSR), and the Defense Threat Reduction Agency (DTRA) intended the study to:

- Identify high-impact research areas worth exploring in U.S. R&D programs
- Clarify research opportunities and needs for promoting progress in the field
- Identify opportunities and mechanisms for international collaboration
- Evaluate the position of foreign research programs relative to those in the United States

The sponsors agreed to maintain the same general framework as that of the 2003 NSF workshop, with an added emphasis on applications. Thus, there were four topical focus areas of the WTEC study:

1. Design and control of synthetic catalytic structures
2. Nanoscale characterization of catalysts in their working state
3. Theory and simulation
4. Applications

APPROACH AND METHODOLOGIES

WTEC recruited a panel of eight U.S. experts in the field, chaired by Robert Davis of the University of Virginia, to perform the assessment. Table 1.1 provides a list of the panelists and their areas of focus for the study. The table also shows others who helped arrange, conduct, and evaluate the site visits. Biographies of the panelists are given in Appendix A.

Table 1.1. Key Members of the WTEC Team and their Roles in the Catalysis Study

Name	Organization	Assignment	Technical Focus
Robert Davis	University of Virginia	Panel Chair	General Trends
Vadim Guliants	University of Cincinnati	Panelist	Applications
George Huber	University of Massachusetts	Panelist	Applications
Raul Lobo	University of Delaware	Panelist	Synthesis
Matthew Neurock	University of Virginia	Panelist	Theory and Simulation
Jeffrey Miller	BP Corporation	Panelist	In situ Spectroscopy
Renu Sharma	Arizona State University	Panelist	Electron Microscopy
Levi Thompson	University of Michigan	Panelist	Applications
John Regalbuto	NSF/Engineering	Sponsor/Observer	
Mike DeHaemer	WTEC	Support Staff	
Hassan Ali	WTEC	Support Staff	

A worldwide assessment of this kind normally begins with a benchmarking exercise to establish the state of the art in U.S. R&D programs. In this case, the report from the 2003 NSF workshop on Future Directions in Catalysis: Structures that Function at the Nanoscale served as a reference point for U.S. activities in the focus area of our study. Therefore, the WTEC study was performed in the following four phases:

1. Conduct a bibliometric analysis to establish world trends in publishing in the field. The analysis examined publication trends by various countries over the last decade. Results were used to confirm and identify new sites selected by the panelists to visit. A complete summary of the bibliometric study can be found in Appendix B.
2. Visit a number of the world's leading university, government, and industrial laboratories. The WTEC panelists visited 20 sites in China, Japan, and the Republic of Korea during one week in June of 2007 and 22 sites in Europe during one week in September of 2007. A complete list of those sites is provided in Table 1.2. Obviously, the panelists could not visit all of the major laboratories performing catalysis research in a two-week time frame. In a few cases, panelists met with representatives away from their laboratories, when travel logistics prevented an actual site visit. Site reports from the Asia and Europe visits are provided in Appendices C and D, respectively.
3. Report findings in a public workshop. The panelists reported their findings to the U.S. sponsors, the catalysis community, and the general public at a workshop held at the FDIC L. William Seidman Center in Arlington, VA, on November 29, 2007. The workshop, entitled "Assessment of International R&D in Catalysis by Nanostructured Materials," was a public forum in which panelists presented overall findings, specific examples from the site visits, and general conclusions. The workshop also allowed for discussion and critical review of the findings.
4. Compile the findings into a written report. This document represents the written record of the study that is available to the sponsors, funding agencies, policymakers, the catalysis community, and the general public. Each panelist authored several site reports and a chapter in his or her focus area. The site reports and individual chapters were submitted to the appropriate site hosts for review and possible correction of factual statements, as necessary. This report is available on the Web at http://www.wtec.org/catalysis/.

REPORT STRUCTURE

The report is generally organized along the topical areas outlined by the original 2003 NSF workshop on Future Directions in Catalysis: Structures that Function at the Nanoscale. This first chapter discusses the publication outputs of the various countries compared to the United States, compares some of the funding strategies for catalysis research in various countries, and highlights the major findings of the study. Chapter 2 by Raul Lobo discusses the important role of materials synthesis in current and future research on catalysis by nanostructured materials. Chapters 3 and 4, authored by Jeff Miller and Renu Sharma, highlight the recent advances in characterization of catalysts: Miller emphasizes the critical role of *in situ* spectroscopy in catalysis research; Sharma focuses on the use of new microscopic techniques for direct imaging of catalysts at the nanoscale. Chapter 5 by Matt Neurock discusses the growing use of *ab initio* molecular modeling and simulation in catalysis R&D and how future developments in computational methods can facilitate discovery. Chapters 6 and 7, authored by Levi Thompson and Vadim Guliants, focus on the specific applications of catalysts in production of energy carriers and chemicals from fossil fuel resources; those chapters also discuss catalytic applications aimed at pollution prevention or remediation in the utilization of fossil fuels. The final chapter by George Huber also examines how catalysts are used for energy and chemicals production, but with a particular focus on renewable feedstocks. There are five appendices:

A. Biographies of Panelists
B. Bibliometric Analysis
C. Site Reports from Asia
D. Site Reports from Europe
E. Glossary of Terms and Acronyms

Table 1.2. Sites Visited by the WTEC Catalysis Panel

ASIA

National Institute of Advanced Industrial Science and Technology (AIST; Japan)
Dalian Institute of Chemical Physics, State Key Lab. of Catalysis (P.R. China)
Dalian Univ. of Technology, Key Labs. of Fine Chemical Engineering, Petrochemical Technology (P.R. China)
Hitachi High-Technologies Corp., Naka Application Center (Japan)
Hokkaido University Catalysis Research Center (Japan)
Institute of Coal Chemistry, Chinese Academy of Sciences (P.R. China)
Jilin University, State Key Lab. for Inorganic Synthesis and Preparative Chemistry (P.R. China)
Korea Advanced Institute of Science and Technology (KAIST; R. Korea)
Peking University, Colleges of Chemistry and Chemistry and Molecular Engineering (P.R. China)
Photon Factory, High Energy Accelerator Research Organization (PF, KEK; Japan)
Pohang University of Science and Technology (POSTECH; R. Korea)
Research Institute of Petroleum Processing (RIPP; P.R. China)
Seoul National University School of Chemical and Biological Engineering (R. Korea)
Tianjin University, State Key Laboratory of Applied Catalysis (P.R. China)
Tokyo Institute of Technology, Division of Catalytic Chemistry (Japan)
Tokyo Metropolitan University Department of Applied Chemistry (Japan)
Toyota Motor Corporation, Higashi-Fuji Technical Center (Japan)
Tsinghua University, Inst. of Physical Chemistry, Chemical Engineering Dept., others (P.R. China)
The University of Tokyo, Depts. Of Chemistry and Chemical Systems Engineering (Japan)
University of Tsukuba, School of Pure and Applied Sciences, Inst. of Materials Science (Japan)

EUROPE

Cardiff University, Heterogeneous Catalysis and Surface Science Group (UK)
Denmark Technical University, Center for Individual Nanoparticle Functionality (Denmark)
Eindhoven University of Technology (The Netherlands)
ETH (Swiss Federal Institute of Technology, Zurich) Baiker Catalysis and Reaction Engineering Grp.
Fritz Haber Institute, Departments of Molecular Physics and Chemical Physics (Germany)
Haldor Topsøe A/S, Research and Development Division (Denmark)
IFP/Institut Français du Pétrole (France)
Institute of Catalysis and Petrochemistry (Spain)
Institute Charles Gerhardt Montpellier, Advanced Materials for Catalysis & Healthcare (France)
Institute of Chemical Technology (ITQ; Spain)
Institute of Research on Catalysis and the Environment of Lyon (IRCELYON; France)
Politecnico di Milano and Università degli Studi di Milano (interviews at Univ. of Turin; Italy)
Max-Plank-Institut für Kohlenforschung (Germany)
Shell Global Solutions International BV (The Netherlands)
Technical University of Munich (Germany)
University of Cambridge, Magnetic Resonance Research Center (UK)
University of Cambridge, Department of Chemistry (UK)
University of Messina (interviews at Univ. of Turin; Italy)
University of Milan: Consiglio Nazionale delle Ricerche (CNR) & associated labs (interviews at Univ Turin, Italy)
University Pierre and Marie Curie, Laboratory of Surface Reactivity–CNRS (France)
University of Turin (Torino; Italy)
Utrecht University (The Netherlands)

BIBLIOMETRIC ANALYSIS

WTEC contracted with Grant Lewison of Evaluametrics, Ltd., United Kingdom, to perform the bibliometric analysis; a complete summary of the findings can be found in Appendix B. Lewison met with panel chair Davis at the University of Virginia in April of 2007 to develop a filter capable of retrieving papers appearing in the Science Citation Index (SCI) relevant to the topic of interest. The names of specialty journals (such as *Journal of Catalysis* and *Applied Catalysis*) and recurring title words were used to create the filter. One problem encountered with this approach was the improper retrieval of papers involving homogeneous catalysis or biocatalysis. Thus, specific elements and reactions commonly involved with solid catalysts were added to the filter. Moreover, titles with certain key words or acronyms such as DNA, protein, protease, RNA, and solar cell were eliminated from the search process. Nevertheless, the calibration of our final filter showed a precision of 0.62 and a recall of 0.78, and the results of this calibration were used to scale the output of the catalysis papers by a factor of 0.795 (= 0.62 / 0.78). Please see Appendix B for a detailed description of the filtering process.

Several important quantitative outputs were determined by the bibliometric analysis. First, the catalysis papers published by a particular country were counted for the 10-year period from 1996 to 2005. Compared to the world output of all science papers indexed in the SCI over the same period, catalysis papers represented about 1/60th of the world science output. Perhaps more important, the growth rate in catalysis papers (5.4%) exceeded that of all science papers (2.9%), which suggests a growing importance of catalysis research in the world.

Examining trends by geographic region offers additional insights into global catalysis activities. The output of catalysis papers by 13 Western European countries (Austria, Belgium, Denmark, Finland, France, Germany, Italy, Netherlands, Norway, Spain, Sweden, Switzerland, and United Kingdom) exceeded the total produced by the United States by almost a factor of two. This result is quite significant, since Lewison indicated that the output of the United States and Western Europe is comparable in most other fields of science. Another result of the analysis is the significant growth of catalysis papers from the Peoples Republic of China from 1996–2005. In 1996, the catalysis papers from the United States outnumbered those from China by a factor of 6; however, the large disparity between China and the United States was largely eliminated by 2005. A reasonable extrapolation of the exponential growth of Chinese publication output suggests that the United States may now lag China in the number of catalysis papers. Japan, which is currently the second major producer of catalysis papers in East Asia, had a much more modest rate of increase of catalysis publications compared to China, while the publication rate from the United States was essentially flat throughout the decade under analysis.

A second quantitative aspect of the bibliometric analysis involved a country's Relative Commitment (RC) to catalysis. By definition, the RC is the integer count of catalysis papers divided by the total number of science papers published by that country. Thus, the RC measures the importance of catalysis research within a particular country, with the RC value for the entire world being unity. The very high relative commitment of China (RC > 2) to catalysis research over the last decade is consistent with its exponential growth in published papers. This contrasts a very low commitment of the U.S. to catalysis research (RC ~ 0.6). The relative commitment of Western Europe to catalysis varies by country, but is generally near the world average (RC = 1).

A third quantitative parameter evaluated in the analysis is the Potential Citation Impact (PCI). This parameter was calculated from the citation records of journals publishing the papers retrieved by the filter, assuming catalysis papers in the journals will be cited at the same frequency as other papers. In this particular study, the PCI was based on the expected citations of a paper in the year it was published and the four subsequent years. The papers published by U.S. researchers appear in journals with the highest potential impact (PCI ~13), whereas the papers published in East Asia appear in journals with below-average impact factors (China PCI ~6.5, Japan PCI ~8.0, Republic of Korea PCI ~6.7). The PCI of Western European countries is near the world average of about 9 for the decade of analysis. Although the PCI associated with the U.S. publications exceeds both East Asia and Western Europe, the high research volume of the European countries more than makes up for the difference in PCI. For example, an overall or total citation impact of a

country can be calculated as the product of the PCI and the total number of papers published by a country or region. Figure 1.2 compares the total number of expected citations from papers originating from North America, Western Europe, and East Asia. The figure is consistent with the rapid growth in the number of publications from East Asia compared to the rest of the world. Although East Asian researchers tend to publish in journals with lower impact factors than U.S. authors, the recent high volume of papers from that region resulted in a total citation impact nearly equivalent to that of the United States. Moreover, the total impact of papers from Western Europe dominated the world over the decade under study, and the gap between Western Europe and the United States widened over this time period.

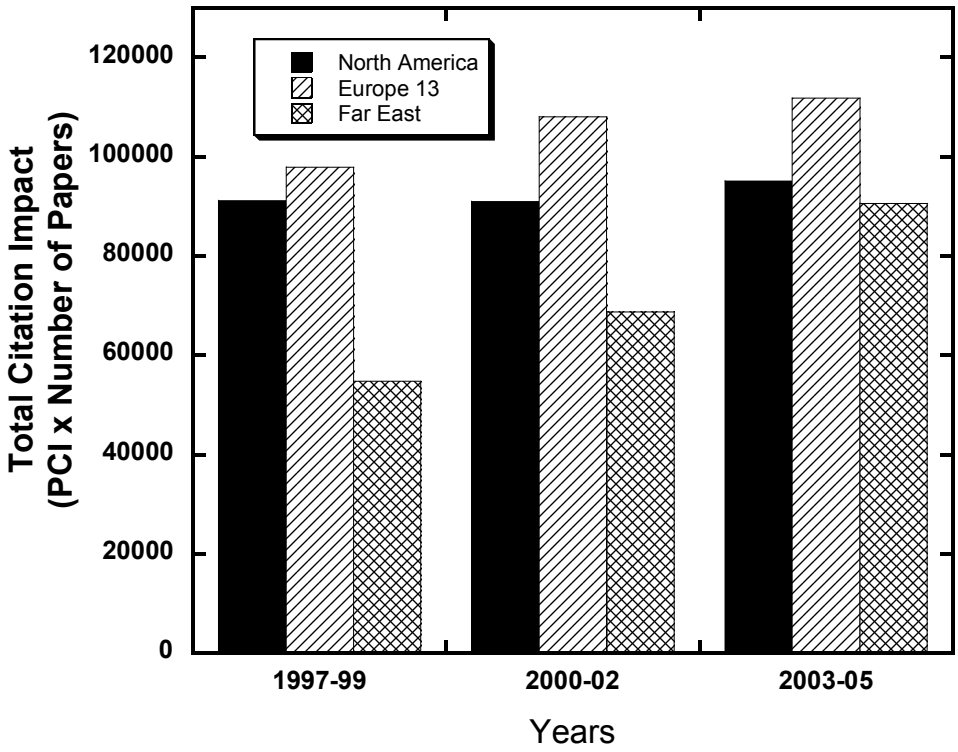

Figure 1.2. Comparison of the total citation impact of various geographic regions.

The National Research Council (NRC) of the National Academies completed a benchmarking study in 2007 of the competitiveness of U.S. research in Chemical Engineering (NRC 2007a) and Chemistry (NRC 2007b). Although heterogeneous catalysis is a subfield of physical chemistry, a significant fraction of catalysis research in the United States is performed in chemical engineering departments. Therefore, the benchmarking studies by the National Research Council explicitly reported on the U.S. position in catalysis with respect to chemical engineering departments, whereas the discussion of catalysis within chemistry departments was indirect through an overall study of physical chemistry. The general findings of the NRC report on chemical engineering are completely consistent with the current WTEC bibliometric analysis. For example, the fraction of U.S. papers published in the leading journals *Journal of Catalysis*, *Applied Catalysis A,* and *Applied Catalysis B* was 33% in the period 1990–1994, but declined to 23% in 1995–1999 and to only 15% in 2000–2006 (NRC 2007a). The citation statistics follow a similar trend. Over the time period of 1990 to 2006, the U.S. share of the top 50 most-cited papers in *Journal of Catalysis* and *Applied Catalysis* A&B fell from 27 (54%) to 12 (24%) (NRC 2007a).

Although the WTEC study did not perform an analysis of patents relevant to catalysis, the NRC report on chemical engineering competitiveness indicates that the share of U.S. patents that originated in the United States declined over the same time period relative to U.S. patents that originated in Asia and the European Union (NRC 2007a). Thus, productivity in catalysis research, gauged by both publications and patents, has shown a fractional decline in the United States relative to the rest of the world.

The results of the WTEC bibliometric analysis suggest that the United States had a significant, but not dominant, position in catalysis research over the last decade. Western Europe led the world in both total number of papers published and the total citation impact. However, the very high relative commitment in East Asia to catalysis research, particularly in China, is illustrated by the exponential growth in the number of published papers in the last decade and will soon challenge the position of both the United States and Western Europe.

INVESTMENT MODELS AND TRENDS

The financial models used to support catalysis research vary widely around the world. The following sections provide examples of how catalysis is supported at some of the sites visited by the WTEC panel.

The United States

As a baseline for comparison, the U.S. National Science Foundation and Department of Energy combined support catalysis research at universities at a level of approximately $30 million per year, with nearly half of that originating from the Basic Energy Sciences program at DOE. The Catalysis and Biocatalysis Program at NSF, together with NSF contributions to special programs such as its Nanoscale Interdisciplinary Research Team (NIRT), Nanoscale Exploratory Research (NER), and Partnerships for International Research and Education (PIRE) programs, add approximately $7 million per year to U.S. university research in catalysis. In many institutions outside the United States, the clear distinction between a national laboratory and a university laboratory, as seen in the United States, is fuzzy. A fair comparison of research support must therefore include the U.S. funding at national laboratories. The total support from the DOE Office of Science, the DOE Technology Offices, other governmental agencies, and companies for catalysis research at the U.S. national laboratories is estimated to be about $45 million. Although there are some aspects of catalysis research funded by the military agencies in areas such as fuel cell power and destruction of hazardous agents, the contribution of these agencies to the public research enterprise was not evaluated in this study. Moreover, energy companies, chemical companies, and catalyst manufacturers also sponsor catalysis research at some U.S. universities. However, the major source of fundamental research support for catalysis in the United States is provided by the Department of Energy and the National Science Foundation.

Asia

Research in East Asia is supported by very different financial models, depending on the country. For example, the cost of a graduate student to a research grant is negligible in the People's Republic of China, since most of the educational costs are covered by other sources. Therefore, the size of research groups can be quite substantial in China. Interestingly, the very select schools in China such as Tsinghua University and Peking University limit student enrollment at all levels, which translates into modest research group sizes at these institutions. Other institutions without strict enrollment caps enable groups to reach as high as 30 students or more. The Dalian Institute of Chemical Physics (DICP) presents another model for catalysis research in China. This multidisciplinary institute of the Chinese Academy of Sciences is home to the State Key Laboratories of Catalysis and Molecular Reaction Dynamics as well as several national projects and spin-off companies. Approximately 500 staff members are involved in catalysis research, along with a substantial fraction of their 800 graduate students. The support for the catalysis operations at the DICP is estimated to be $15 million per year, which is nearly the same as the DOE Basic Energy Sciences catalysis budget or double the NSF catalysis budget for university research across the United States. At nearly every institution visited in China, panelists observed new research equipment being installed in the laboratories.

The financial support for catalysis in the Republic of Korea is mainly distributed through several government programs. For example, graduate students are supported in targeted departments with funds designated for "Brain Korea 21st Century" (BK21). The BK21 program is used to promote academic disciplines of national importance and provides funds for graduate education to top departments in those fields. The chemical engineering departments at Seoul National University and Pohang University of Science and Technology, where most of the catalysis research is performed at those schools, participate in the BK21 programs and receive support for most of the costs associated with graduate students. Another government program

funding catalysis research in Korea is the National Creative Research Centers, which forms 5 new research centers every year after a country-wide competition in all fields of science. Funding for these centers is provided for up to 9 years. One such center, the Korea Advanced Institute for Science and Technology (KAIST) Center for Functional Nanomaterials, is supported at ~$700,000 per year. Finally, research grants from the Korean Science and Engineering Foundation are a significant source of support for university catalysis researchers.

Funding for catalysis research at Japanese universities is provided mostly by various Japanese government agencies. For example, the University of Tokyo receives only 20–30% of its external funding from the Japanese chemical industry, with the rest presumably originating from government sources. The research funding per full professor at the University of Tokyo is about $600–800 thousand, not including summer faculty salary, student stipends, tuition, and overhead. Since the Japanese government provides funding directly to graduate students for stipends and tuition, the external research funds raised by faculty can be used for a variety of needs in the laboratories. The Japanese Ministry of Education, Culture, Sports, Science and Technology recently established a fund to create "The 21st Century Centers of Excellence" program, which covers all academic fields and gives priority support for global research and education centers. Almost a quarter of University of Tokyo professors participate in this program. In addition to the catalysis research at universities, Japan also supports the activities at national laboratories such as the National Institute of Advanced Industrial Science and Technology (AIST), which is the largest public research organization in Japan. Catalysis plays a central role in several of the research themes within the institute, including centers in Biomass Technology, Hydrogen Industrial Use and Storage, and New Fuels and Vehicles Technology, as well as institutes on Innovation in Sustainable Chemistry and Energy Technology. The Institute for Innovation in Sustainable Chemistry had a total budget in FY2006 of $18.2 million for a technical staff of 86 scientists, 35 postdoctoral researchers, and 60 technicians.

Western Europe

Support for catalysis research in the European Union varies widely by country and by institution. The Fritz Haber Institute (FHI) in Germany is funded primarily (~60%) by the Max Planck Society, with grants from the German Science Foundation, the European Union, and other sources making up the rest. Only about 5% of the Fritz Haber Institute's catalysis research budget is derived from industrial sources, with most of those funds being directed to the catalysis research in the Department of Inorganic Chemistry. The overall annual budget for personnel and operating costs at the FHI is $35–40 million, which supports 5 director positions, 148 technical staff positions, 80–100 Ph.D. students (many with outside funding), and 35 support staff. Although the FHI pursues fundamental research in a variety of fields, the institute has a current focus on catalysis, chemical and physical properties of interfaces, molecules, clusters, and nanostructures. In contrast to the FHI, the catalysis activities at the Technical University of Munich are funded by competitive government grants, noncompetitive government support, and industrial contracts, shared almost equally among the sources.

Catalysis research in Spain is focused at the Institute of Catalysis and Petrochemistry (ICP) in Madrid and the Institute of Chemical Technology (ITQ) in Valencia. Both institutes are funded by the Spanish Council for Scientific Research (CSIC) at substantial levels. The ICP is the largest catalysis research institution in Spain and consists of 4 departments: Structure and Reactivity, Applied Catalysis, Catalytic Process Engineering, and Biocatalysis. To provide a sense of scale, the Structure and Reactivity department has an annual budget of about $2 million, half of which is provided by the CSIC. The department supports 10 staff scientists, 4 postdoctoral researchers, 17 PhD students, 4 contracted graduate students, and an administrative person. The ITQ has a staff of about 100 people (64 researchers and technical staff members, 28 doctoral students, and 21 postdoctoral researchers) supported by an annual budget of about $6 million. The unique financial structure of the ITQ has enabled fantastic expansion from its inception in 1991 and accounts for about 600% growth in income over the last decade. Almost 60% of that income is derived from contracts with companies and licensing fees generated by patents developed at ITQ.

The French government has established the following 7 priority areas of research for its country: (1) Biology and Health; (2) Ecosystems; (3) Energy and the Environment (including CO_2 minimization, hydrogen and

fuel cells, bioenergy, transport, and clean vehicles); (4) Engineering Processes (including chemistry and processes, materials and processes); (5) Physics and Information; (6) Humanities and Society; and (7) Basic Science (Chemistry and Multidisciplinary Studies). Although catalysis has a major role in 3 of the 7 priority areas and is clearly a field with substantial support in France, there was an indication that research funding may decline in the future. Nearly a third of academic catalysis research in France occurs at the Institute of Research on Catalysts and the Environment of Lyon (IRCELYON). The annual budget for IRCELYON is ~$16 million, with over half of that budget dedicated to 113 permanent positions funded by the Centre National de la Recherche Scientifique (CNRS), government, and the University of Lyon. The rest of the budget is for equipment, supplies, and support for 68 PhD students and 23 postdoctoral researchers. A completely different model for catalysis research is practiced by the Institut Français du Pétrole (IFP). The IFP performs both technology development (75%) and basic research (25%), and serves as an interface between academic and industrial groups. It is supported by the French government (two-thirds) and licensing revenues (one-third) from inventions developed at the institute. About $60 million of the annual budget is dedicated to catalysis research in support of the activities of 200 staff members and about 60 PhD students.

The Netherlands and Denmark have made substantial recent investments in catalysis research. For example, The Netherlands Organization for Scientific Research selected the National Research School Combination-Catalysis (NSRC-Catalysis) in 1998 as one of six special programs to be funded in a competition with all fields of science. This program supported catalysis research activities at 8 different universities over the last decade and has been renewed at multimillion-dollar-per-year levels through 2013. Last year, the program supported the activities of 50 researchers, with doctoral and postdoctoral researchers comprising the majority of the personnel. Very recently, the Netherlands Institute for Catalysis Research (a virtual institute for catalysis research and education) was awarded a center grant in the area of bio-renewables conversion for more than $40 million over the next eight years. The center, called CATCHBIO, couples universities across the Netherlands with a variety of industrial collaborators. The catalysis activities in Denmark are focused at the Technical University of Denmark (DTU) and collaborations with close-by Haldor Topsøe. The research is directed by several well-funded centers at DTU, including the Center for Atomic-Scale Materials Design (CAMD) and the Center for Individual Nanoparticle Functionality (CINF). The funding for CAMD, which is generally recognized to be one of the world's leading centers in computational catalysis, is reported to be $14 million over the 2006–2011 time period, excluding computer grants and funds for permanent staff of 7 faculty members and 6 support persons; over one-third of the support is provided by the Lundbeck Foundation. The CAMD has 8 faculty members, 12 postdoctoral researchers, 17 PhD students, and 7 support persons.

Italy has about 500–600 catalysis researchers in catalysis that participate in a variety of national and European consortia. The Interuniversity Consortium for the Science and Technology of Materials is comprised of 44 universities performing research in materials science in connection with chemistry, engineering, and nanotechnology; one of the eight section topics of this consortium is relevant to catalysis and reactive interfaces. The estimated budget for the catalysis activities is about $2 million per year. Also, Italy participates in the European IDECAT initiative (Integrated Design of Catalytic Nanomaterials for a Sustainable Production), which was formed in 2005 and is funded at approximately $14 million over a five-year period. IDECAT involves 37 laboratories from 17 institutions in 12 countries with about 500 participants overall and has goals to integrate top-level EU expertise in catalysis and to create a critical mass of researchers that will enable a step-change in catalysis R&D in Europe.

The United Kingdom has about 6 groups substantially involved with catalysis and surface science; the WTEC team visited sites at Cardiff University and Cambridge University. The 65 people at Cardiff University (7 academics, 13 postdoctoral researchers, and 45 students) are funded by more than $10 million in external grants, which are derived primarily from government sources (60%) and the rest coming from industrial contracts. The Surface Science activities at Cambridge University are supported by over a $1 million per year by the government, with additional industrial grants, to support a total staff of 1 senior professor, 1 research fellow, 7 postdocs, and 11 PhD students.

Summary

The different financial models used throughout the world are effective at supporting catalysis research; no single system can be declared as the best. However, certain aspects of each deserve close examination for possible adoption in the United States. For example, the sustained level of baseline funding provided to a science-oriented institution such as the Fritz Haber Institute allows for effective utilization of the highly trained research staff that is necessary to build the world's next-generation scientific instruments. However, a stable funding stream is not the only unique feature that allows the institution to function at a very high level scientifically. Justification of research directions at the FHI is based on a recommendation from an external evaluation committee of scientific experts from around the world instead of classical numerical outputs such as papers and patents. This stable source of funding for long-term research goals at the FHI contrasts with the typical three-year granting cycle at the U.S. government agencies, which also require yearly justifications for grant expenditures. This difference in funding strategy between the U.S. government and the FHI was highlighted during the WTEC visit as a major reason why certain kinds of research and instrument development are unique to the FHI.

The consortia model developed within and throughout the European countries is another strategy for funding research. These consortia tend to be most effective within a single country, presumably because of the ease of communication, shared cultural identity, and geographic proximity of participating institutions. Although pan-European initiatives have also experienced success, a significant fraction of funding in those initiatives is dedicated to travel and collaboration instead of directly supporting research.

The European and Asian countries have done an excellent job combining academic research with national laboratory activities. The combination is almost seamless at many institutions, with principal investigators, professors, doctoral students, and research staff members working together on common goals. There appears to be a more significant separation between academic catalysis research in the United States and its complement at the mission-oriented DOE national laboratories.

The support of doctoral students and postdoctoral researchers on U.S. research grants tends to consume the major fraction of direct charges. In countries like China and Korea, government programs that fund students directly for their graduate education in areas of national importance remove the need to fund students directly on research grants. Although it is unclear whether or not that system is superior to funding students directly on grants, it does appear to be similar to the graduate training grant programs in the United States that are common in other fields.

The WTEC panelists found significant industrial collaborations at most of the sites and had the impression that industrial support is more prevalent outside of the United States. The reasons appear to be many, such as a lower cost of performing research outside of the United States, a more cooperative intellectual property environment outside of the United States, and possible access to emerging world markets for the next users of catalytic technologies. Moreover, the panel noted the high quality of pilot plant facilities and catalytic reactor systems capable of industrial operating conditions located within academic settings. The infrastructure for fundamental research on catalyst synthesis and characterization combined with industrially relevant catalyst testing appears to exceed that of typical academic catalysis laboratories in the United States.

Routine equipment for catalysis research such gas chromatographs, reactors, vacuum chambers, adsorption systems, bench-top spectrometers, as well as major research instruments such as electron microscopes, nuclear magnetic resonance spectrometers, and X-ray diffractometers is well represented worldwide. In addition, researchers appear to have ready access to synchrotron light sources for advanced *in situ* characterization of catalysts. However, the panelists reported a significant concern with the aging catalysis infrastructure in the United States compared to that observed in East Asia and Europe. The difficulty U.S. researchers currently have with acquisition of new instruments routinely used for catalysis research could severely impact U.S. competitiveness in the very near future.

GENERAL OBSERVATIONS

As stated in the NRC report on chemical engineering competitiveness, catalysis is often associated with large-scale chemical, petrochemical, or oil refinery processes, which are areas of rapid growth in Asia but are fairly stagnant in the United States and the European Union (NRC 2007a). Although Asia's rapidly expanding economy accounts for its major growth in catalysis research, the reasons for the dominant position of Western Europe in catalysis research output are not so straightforward.

Several key factors are likely to contribute to this result. First, catalysis is generally viewed outside of the United States as a fundamental science that enables discovery and development of technology in a variety of energy- and chemicals-related fields. Therefore, catalysis research is pursued in chemistry and physics departments throughout Europe, with much smaller levels of activity in European chemical engineering departments. Within the United States, heterogeneous catalysis has been viewed as a mature field that is studied mainly in chemical engineering departments. Chemistry departments in the United States tend to support much more fundamental studies involving model surfaces in pristine environments, homogeneous or single-site molecular catalysis, and biocatalysis. This artificial division may allow heterogeneous catalysis in the United States to be incorrectly perceived as an applied field of research instead of one with the potential for fundamental discovery.

Another reason European catalysis appears to have a dominant position is the close coupling in Europe of universities and national laboratories with industry. Companies within several of the countries the WTEC panel visited appear to campaign for catalysis research at the national level. This kind of advocacy support from companies, together with research contracts involving universities and government labs, indicates a significant role of the private sector in setting research directions. Moreover, the current intellectual property environment in Europe appears to foster university-company relations, at least more so than in the United States. However, there are indications that European universities are beginning to explore the position of many U.S. universities on IP ownership and may soon move in the direction of the United States where universities routinely negotiate for ownership of IP.

Finally, the overall level of investment in catalysis research in Europe simply appears to be higher than that in the United States. Although the United States is starting to see large block grants from companies such as BP and the Dow Chemical Co. for catalysis research at universities, the combined investment of the U.S. government (mainly NSF and DOE) and the industrial sector in university and national laboratory research appears to be far below that of the European countries.

The WTEC panelists observed the use of high-throughput instrumentation in both Asia and Europe. For example, robotic synthesis of zeolite materials and high-throughput reaction testing allowed for discovery of new catalytic materials with unique properties at the ITQ in Valencia, Spain. Also, the Center for Microchemical Process Systems at KAIST in Korea makes extensive use of high-throughput screening methods for discovery of new materials. New instrumentation recently purchased at institutions throughout Asia and Europe was aimed at rapid analysis of catalyst samples. Since research abroad is often carried out in major centers of activity, some of the instrumentation was actually invented and constructed in-house. This model contrasts with the operation of most academic laboratories in the United States, which have neither in-house expertise for tool creation nor the resources for tool construction.

The panel also noted the effective use of permanent research staff positions in laboratories outside of the United States. In the vast majority of sites visited, including those associated with institutes and universities, the number of dedicated staff members in support of the research activities appeared to far exceed those associated with U.S. laboratories. The employment of highly skilled technical staff members at the Fritz Haber Institute was highlighted during the visit as a major reason why next-generation research instruments can be designed and built within the facility. The instruments were too complex to be constructed solely by graduate students and short-term postdoctoral researchers. The current funding models in the United States do not support the same level of technicians, and academic institutions do not appear to have funds available for additional positions; in fact, many U.S. researchers are experiencing a decrease in technical staff at their universities.

TECHNICAL THEMES OF THE STUDY

The subsequent chapters in this report present the findings of the panel with respect to the four technical themes of the study: synthesis, *in situ* characterization, theory and simulation, and applications. Regarding catalyst synthesis, new methods to produce highly structured solids such as zeolites and carbons having both micropores and mesopores were being actively pursued in several countries. Moreover, preparation and stabilization of metal and metal oxide nanoparticles with controlled facets, sizes, and compositions are also areas of wide interest. Characterization of nanostructured catalysts by environmental electron microscopy is revealing how nanoscopic features are affected by the surrounding environment; this advanced method of observation will be pursued more aggressively with the increasing availability of commercial instruments. *In situ* spectroscopy has now become a routine method for catalyst characterization around the world. However, rapid improvements in temporal and spatial resolution of many spectroscopic methods as well as adaptation of methods to allow for interrogation of catalysts under industrial reaction conditions are enabling an unprecedented level of new information to be collected on the structure of catalysts in their working state. Theory and modeling have gained universal acceptance as necessary tools for advancing catalysis science. Improvements in method accuracy, computational speed, and model development have moved theory to a position alongside experimentation in many laboratories. Theory has excelled in the prediction of atomic structure and spectroscopic features of catalytic materials. Although the prediction of reaction kinetics is still developing, theory is being used to suggest novel compositions to improve catalytic performance.

The key applications stimulating most of the catalysis research worldwide were related to energy and the environment. Conversion of nonpetroleum feedstocks such as coal, natural gas, and biomass to energy and chemicals was a high priority in nearly all of the countries visited. China, in particular, has a major emphasis on energy applications, especially those involving the conversion of coal to liquid fuels. Significant activities in photocatalysis, hydrogen generation, and fuel cells are carried out in many locations. There is a general recognition that energy carriers and chemicals should be produced, and ultimately used, with as little impact on the environment as possible; catalytic solutions are thus being pursued in this framework of environmental sustainability. Catalytic production of ultra-low sulfur fuels, use of renewable carbon sources and sunlight, conversion of the greenhouse gas CO_2 to useful products, highly selective oxidation of hydrocarbons, and catalytic after-treatment of waste streams are all being pursued vigorously around the globe. A growing area of interest is the catalytic transformation of various plant sources to energy-relevant compounds such as bio-oil (a carbonaceous liquid that can be blended into a refinery stream), biodiesel fuel, hydrogen, alcohols, and so forth. However, the targeted plant feedstocks depend on the native vegetation within a particular country.

CONCLUSIONS

Catalysis by nanostructured materials is an active area of research around the globe. Its rate of growth appears to be increasing faster than that of all science, presumably because of significant concerns regarding future energy security and environmental sustainability. Western Europe currently holds a dominant position in the world in terms of research paper output, but the rapid growth of research in Asia over the previous decade could challenge that position in the near future. The overall investment levels in catalysis research in Western Europe and Asia appear to be significantly greater than that of the United States. Since recent U.S. publications are the highest-cited in the world, research funds in the United States are distributed effectively to the highest-quality laboratories. The overall impact of U.S. research, however, is dampened by a much smaller output relative to Western Europe and the growing output from Asia. The technical themes involving catalyst synthesis, characterization, theories, and applications have specific components that are similar to those in U.S. research programs, but the level of research activity in particular areas often depend on regional needs.

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CHAPTER 2

SYNTHESIS OF NANOSTRUCTURED CATALYSTS

Raul F. Lobo

INTRODUCTION

As defined in Chapter 1, "a heterogeneous catalysis is a molecular event occurring at a solid-fluid interface [where] the nanostructure surrounding the reactive interface, known as the active site, can significantly influence the observed rate of reaction (referred to as catalytic activity) and the distribution of observed products (known as selectivity)." This definition points to the need to control the molecular structure of a heterogeneous catalyst at the nanometer length scale to successfully prepare catalysts that are both active and selective. The catalysis community endeavors to accomplish this objective by the creative use of diverse synthesis methods. This chapter describes important examples of successful control of catalyst nanostructure and its impact on catalytic activity and selectivity, as observed by the WTEC panel during its visits to laboratories in Asia and Europe. The aim of this review is not to be exhaustive, but rather to illustrate the innovative ways in which scientists and engineers are successfully controlling atoms and molecules to self-organize in cooperative assemblies with meaningful catalytic functions. The selected examples of nanostructured catalysts described here are ones that have shown interesting or unique activities.

The definition of heterogeneous catalysis given above does not reveal the difficulty of the task that is the preparation of successful and novel catalysts. In particular, in addition to catalytic activity and selectivity, practical catalytic materials must be very stable at reaction conditions. Practical industrial reaction conditions often require high temperatures and strong oxidizing or reducing environments—environments that must be withstood for extended periods of time by the nanostructured catalysts. In addition to structural stability, long-term catalytic activity requires that impurities (either in the feed or by-products of the reaction) do not accumulate on the catalyst surface and block access by the reacting molecules to the active site. This chapter discusses mainly the activity and selectivity of novel nanostructured catalytic materials because these are the properties readily controlled through synthesis. The issues of stability are nevertheless important and are discussed in more detail in other chapters.

First, some context and definitions are provided here for some of the ideas discussed later by describing an example of a nanostructured industrial catalyst already used in industry, platinum (Pt) nanoparticles supported on zeolite K-L (Treacy 1999). This example epitomizes the importance of nanoscopic length scales in catalytic materials and is one to which other materials described below can be compared. Zeolite L has a one-dimensional pore system with pore windows of ~7.5 Å and cages between the windows of ~11 Å. This material is an excellent catalyst for the reforming of n-hexane and n-heptane into benzene and toluene (McVicker et al. 1993), and it is used commercially for this purpose in several oil refineries. The presence of Pt nanoparticles in the pores of this zeolite is revealed by Z-contrast TEM in the left image of Figure 2.1. This figure also illustrates the diversity of Pt clusters in the zeolite pore (right image of Figure 2.1) in the fresh catalysts. After time-on-stream, the smaller particles aggregate to make particles similar to type B or H. The right side of Figure 2.1 also illustrates that a portion of the active sites can be inaccessible to reacting molecules if two large clusters block the one-dimensional pores of the zeolite. There is then an optimal

loading of metal on the catalysts that depends on the average crystal size of the zeolite support. In the best-case scenario, there will be one metal cluster per pore in each of the crystal pores.

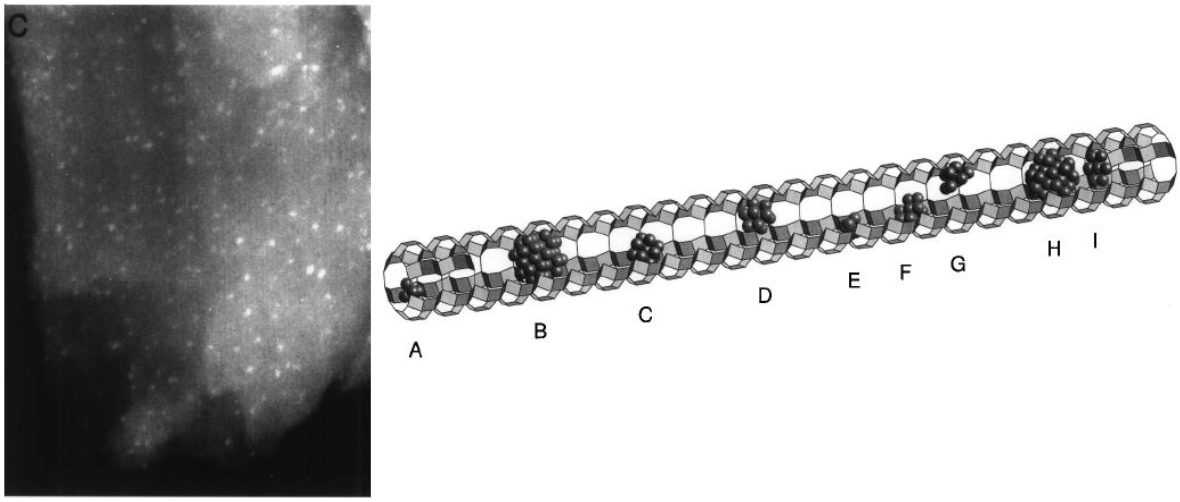


Figure 2.1. (*Left*) A Z-contrast TEM image of zeolite Pt/K-L after reduction and reaction in oil; (*right*) illustration of the location and variable size of Pt clusters in the zeolite pores. In the optimum catalyst, each pore will contain only one particle (of the type B or H) in the pores to maximize access to the active metal surface (Treacy 1999). As depicted, clusters B and H block access to the clusters C-G.

Pt/Zeolite L catalysts are prepared by impregnation, where cationic mononuclear Pt species are dissolved in water and added to the zeolite support. The nanoparticles are formed upon heating this sample in a reducing atmosphere (McVicker et al. 1993). During the heating and reduction, the cationic species migrate into the zeolite pore, decompose, and are reduced. Platinum clusters are formed by migration and aggregation of Pt atoms. Where is the nanostructure "design" in this synthesis? In this case, it is the selection of the zeolite with the precise pore size and shape, and the composition needed to stabilize metal clusters in the pores. The Pt clusters do indeed self-assemble from the molecular species during the activation process. Choosing the "right" zeolite and the proper activation protocol are essential steps to make this nanostructure possible. It must be recognized, too, that in this system the thermodynamically favored state is the formation of large metal particles on the outside of the zeolite crystal. The synthesis process is crucial to capture the metastable disperse nanoparticle phase for long periods of time and to avoid the direct conversion of the precursors into large metal particles.

In the examples of catalyst synthesis that follow, self-assembly of inorganic precursors on a nanostructured support, or the use of self-assembled moieties (such as micelles and rods), are exploited in various ways to achieve materials with novel structures and with interesting catalytic properties arising from the new structure. Self-assembly of molecular entities plays a role in almost every case and can be thought of as the paradigm that connects the diverse materials and synthesis methods discussed throughout.

RHENIUM CLUSTERS IN ZEOLITE ZSM-5

Prof. Iwasawa at the University of Tokyo (see site report, Appendix C) recently reported a new rhenium-based catalyst with exceptional selectivity for benzene hydroxylation to form phenol using molecular oxygen as the oxidant (Bal et al. 2006). The catalyst is prepared by a chemical vapor deposition method using trioxomethylrhenium as the precursor. This rhenium precursor reacts with the acid sites of the zeolite, forming isolated species of rhenium trioxide bound to the zeolite framework. The catalyst is then activated in the presence of ammonia, leading to a reorganization of the intracrystalline rhenium forming isolated Re clusters. The highest selectivity is obtained by flowing a small amount of ammonia along with benzene and oxygen, and the only by-product detected is CO_2.

Both zeolite structure and composition are very important to form the selective Re clusters. Zeolites beta, mordenite, ZSM-5, and USY were investigated, and only the catalysts prepared on zeolite ZSM-5 showed high activity and selectivity. The composition is also very important, because the selectivity of the catalysts increases as the amount of aluminum in the ZSM-5 framework increases (from 48% to 88% selectivity) (Tada et al. 2007). An extended-X-ray absorption spectroscopy investigation of the samples and their evolution with pretreatment revealed that the initially mononuclear species aggregates upon heating and—in the presence of ammonia—forms a very well defined rhenium oxynitride cluster (Figure 2.2). The rhenium assemblies are edge-sharing octahedra with nitrogen atoms in the center and oxygen atoms capping the corners.

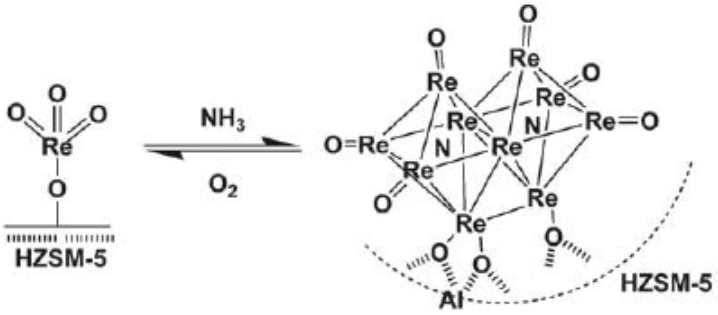


Figure 2.2. Rhenium oxynitride clusters form in H-ZSM-5 zeolites in the presence of ammonia (Bal et al. 2006).

The complex has formally a positive charge and is anchored to the zeolite by electrostatic forces. This structure shows why a small ammonia pressure is required to maintain high activity and selectivity with the cluster. The ammonia provides enough nitrogen background pressure to keep the stabilizing nitrogen atoms in the cluster from leaving the active sites. If the flow of ammonia is stopped, the clusters eventually decompose and catalytic activity is lost. Again, it is important to recognize that only ZSM-5 gives acceptable catalysis levels. It is a zeolite that incidentally turned out to have the most suitable channel dimensions to allow the growth and assembly of the rhenium into a 10-unit cluster—but no bigger. Could this have been predicted from the outset? Probably not, because it was not known *a priori* what the structure was of the active site. The catalyst was prepared following a hint from previous reports suggesting rhenium inside zeolites could be a selective catalyst for benzene hydroxylation (Kusakari, Sasaki, and Iwasawa 2004). By the systematic use of well-organized synthesis techniques (CVD, impregnation, etc.) and activation protocols, Iwasawa's group discovered this very interesting material. It was the combination of good chemical intuition and a well-organized synthesis research plan that allowed them to find this outstanding example of nanostructured catalysis.

NOVEL PROPENE PARTIAL OXIDATION CATALYSTS

The selective oxidation of hydrocarbons accounts for about 25% of the organic chemical products manufactured worldwide. Among the most important types of heterogeneous catalysts used for these oxidations are mixed metal oxides. Mitsubishi Chemicals has developed a new mixed metal oxide catalyst of composition MoVTe(Sb)NbO, a material capable of catalyzing the selective oxidation of propane to acrolein (Grasselli et al. 2003). In a recent report (Sadakane et al. 2007), Ueda and coworkers at Hokkaido University (see site report, Appendix C) describe the synthesis of a new material with many structural similarities to the Mitsubishi catalyst. The basic structure of the Mitsubishi catalyst is depicted in Figure 2.3a. Here, 6- and 7-ring pores are bounded by $\{MO_6\}$ octahedral and pentagonal $\{(M)M_5O_{27}\}$ units that are comprised of a heptagonal $\{MO_7\}$ unit surrounded by edge-sharing $\{MO_6\}$ octahedra (DeSanto et al. 2004). Each unit cell contains four 7-ring pores and four 6-ring pores.

The new structure discovered by Ueda's group is comprised of the same building units arranged with a different connectivity. The result (Figure 2.3b) is a material also containing 6- and 7-ring pores. The new structure has three 7-ring pores and only two 6-ring pores per unit cell, the result of a different concentration

of the $\{MO_6\}$ octahedra with respect to the pentagonal units. The catalytic tests performed on both catalysts show that their activities are remarkably similar for the acrolein–to-acrylic-acid reaction (the 2nd step in the propene oxidation process). These similarities indicate that the layered structure and the presence of both 6 and 7 rings are important to achieve high activity and selectivity at low temperatures. Crude Mo_xV_y oxides were much less active for this reaction.

A Raman and UV/Vis investigation of the synthesis and assembly of the tetragonal and trigonal catalysts reveals important details about the formation of intermediate building units during the synthesis process. These studies show that by controlling the pH carefully during the synthesis of the materials, pentagonal units $\{Mo(Mo)_5\}$ are formed in the precursor solution. This conclusion is inferred from the Raman signatures of the solution, consistent with the formation of polyoxomolybdates that contain the pentagonal unit. UV/Vis spectra are also consistent with the presence of polyoxomolybdates containing the pentagonal unit. These studies show that synthesis of the tetragonal and trigonal catalysts depends on the formation of nanoscale building blocks that can self-assemble into an ordered solid upon the hydrothermal treatment of the synthesis solution.

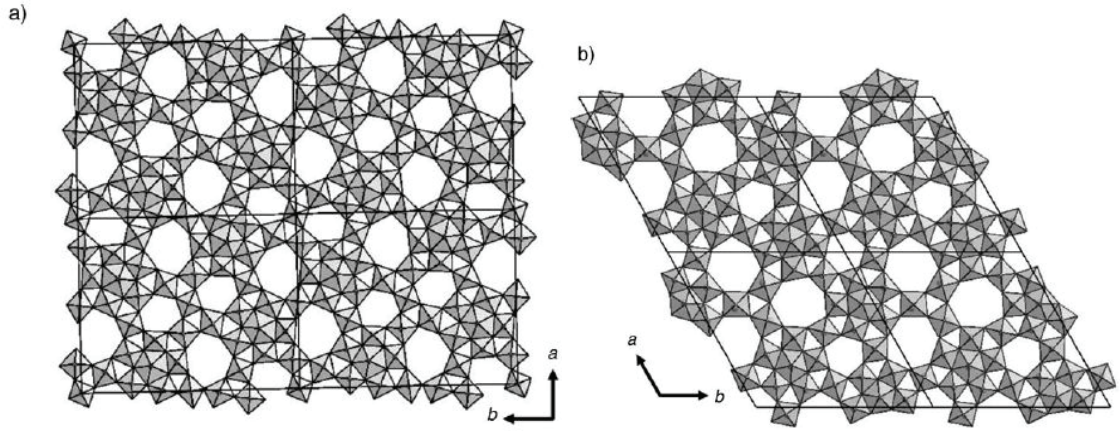


Figure 2.3. (a) Tetragonal structure of mixed metal oxide Mitsubishi catalyst; (b) newly discovered trigonal mixed metal oxide discovered by Ueda at Hokkaido University (Sadakane et al. 2007)

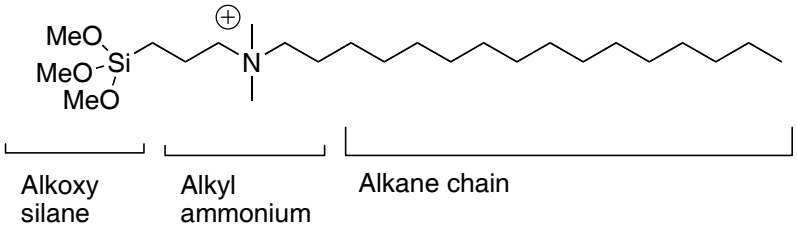
MESOPOROSITY DESIGNED INTO MICROPOROUS CATALYSTS

Selective heterogeneous catalysts usually operate with high selectivity only within a narrow temperature window. Below some minimum temperature, chemical reactions proceed too slowly to be of practical value. Above an effective maximum temperature, secondary reactions become kinetically dominant and make the catalyst impractical. In zeolites and other microporous catalysts, the temperature window of operation for catalytic chemistry is coupled to transport (physical) processes. That is, sometimes the reactants or products diffuse slowly within the catalyst particles, greatly reducing the effectiveness of the catalyst.

This problem is widely recognized as a practical limitation to the application of zeolites, and many attempts and strategies have been devised to overcome it. The obvious one is to reduce the size of the crystallites. This often works, but crystal size reduction also decreases the thermal stability of the zeolite and increases the ratio of external/internal surface areas, promoting unselective reactions that occur on the crystal exterior. Recently, much effort has gone into developing materials that are microporous at one level but also mesoporous at another level, such that the resistance to diffusion is drastically reduced. During visits to Asia and Europe, the WTEC panel observed various strategies to form meso-microporous materials, a promising approach to solve this problem.

Micro-Mesoporous Zeolites by Design of Organic-Inorganic Surfactants

The group of Prof. Ryoo of the Korea Advanced Institute of Science and Technology (KAIST; see site report in Appendix C) has developed an innovative strategy for the synthesis of zeolite crystals containing within them mesoporous channels (Choi et al. 2006). The key developments are the design of a new structure-directing agent containing an alkoxysilane moiety to anchor the molecule to the zeolite, a quaternary ammonium group to provide solubility in the synthesis gel, and an alkyl chain to promote aggregation of the organic structure directors. Scheme 2.1 shows an example of a prototypical molecule used by the Ryoo's group.



Scheme 2.1. Prototypical molecule.

Using this approach, the Ryoo group has been able to prepare several zeolite materials with extraordinary crystal mesostructure. Figure 2.4 shows a typical example of the dramatic change that is obtained in crystal mesostructure. The classical ZSM-5 morphology has particles with a "coffin" shape and with very smooth surfaces (Lai et al. 2003), completely different from the morphology of Figure 2.4.

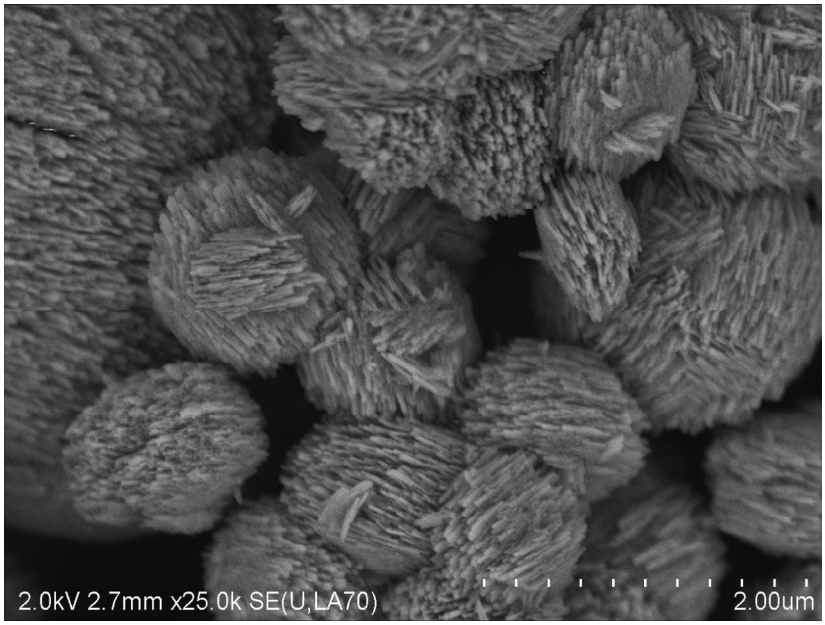
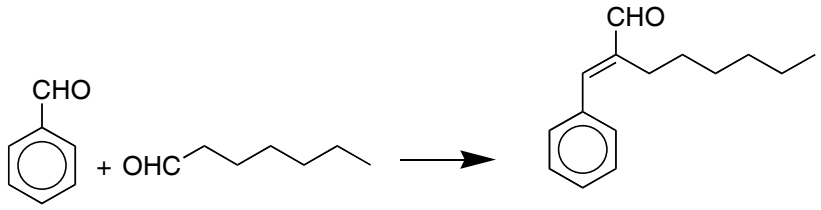


Figure 2.4. Example of the crystal morphology of zeolite ZSM-5 obtained using an organic structure-directing agent similar to the one depicted in Scheme 1 (courtesy of Ryong Ryoo, KAIST).

Analysis of the mesoporosity of these materials using adsorption studies clearly shows highly monodisperse pores, consistent with aggregation of the surfactant structure-directing agents into rods as the zeolite crystal grows towards its final shape. Further indication of the order of the mesoporosity is obtained from X-ray powder diffraction studies that show a relatively narrow peak at low angles (less than 1° 2Θ). This peak arises because of the correlation between center-to-center distances of contiguous mesopores.

Perhaps the most dramatic effect is observed on the catalytic selectivity and activity of these materials (Srivastava, Choi, and Ryoo 2006). One of the reactions where these new materials have shown promise is in the synthesis of jasminaldehyde. Scheme 2.2 shows the reaction of interest starting from benzaldehyde and heptanaldehyde. A mesoporous ZSM-5 zeolite shows excellent activity and selectivity (98% and 98%, respectively) towards the formation of jasminaldehyde (Choi et al. 2006; Srivastava, Choi, and Ryoo 2006). These numbers can be compared to traditional H-ZSM-5 zeolites (3.9% activity and 69% selectivity) and mesoporous aluminosilicates (MCM-41-type materials) that have still lower activity (25%) and lower selectivity (79%) than the mesoporous zeolites. This difference in activity indicates not only that the mesoporosity of the material helps increase catalytic activity, but also that there is some structural change on the mesoporous crystal surface (external to the micropores, but internal to the mesopores) that allows for this large improvement in catalytic selectivity. The synthetic approach developed by the KAIST group is very flexible. At this point, it seems that only a small portion of many structural variations of the molecules have been explored. This is a promising route to discovering new nanostructured catalysts with improved selectivity and activity.



Scheme 2.2. Synthesis of jasminaldehyde using mesoporous zeolites.

Micro-Mesoporous Zeolites from Carbon Templates

Christensen and coworkers at the Technical University in Denmark (see site report in Appendix D) have developed a completely different approach to making zeolite catalysts containing mesopores (Kustova, Hasselriis, and Christensen 2004; Christensen et al. 2005; Christenson et al. 2007). The approach is called the carbon templating method, whereby zeolites are synthesized using a highly concentrated gel in the presence of carbon materials such as carbon black particles (~12 nm in diameter), carbon fibers, carbon nanotubes, etc. During crystal growth, zeolite crystals grow around the carbon structures in the synthesis gel, engulfing the carbon particles. After the zeolite synthesis has been completed, the samples are heated in the presence of oxygen and the carbon is burned completely, leaving spaces within the crystal with irregular orientations and locations but relatively uniform in size. The TEM image in Figure 2.5 is of a crystal of ZSM-5 after calcination and removal of the carbon. The mesopores can be observed clearly in the image. This method is very flexible and is widely applicable to the synthesis of many zeolite structures. It can yield a large fraction of mesoporous volume (up to 1.0 cc/g).

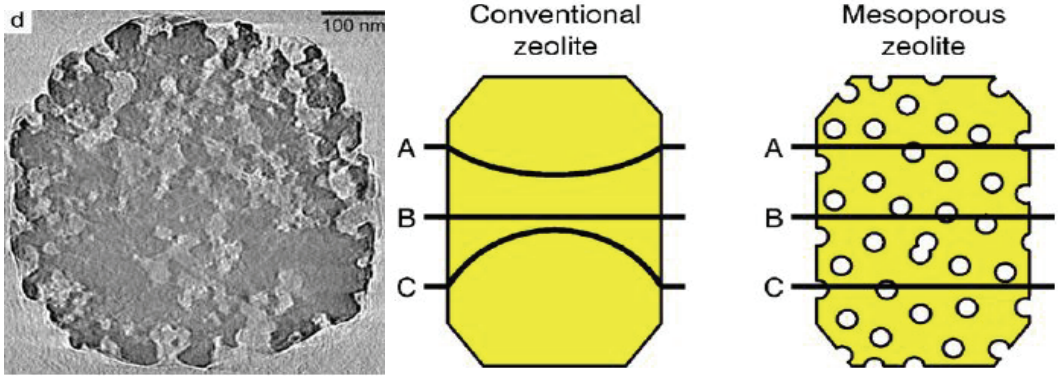


Figure 2.5. (Left) TEM image of zeolite silicalite-1 prepared using carbon black particles in the synthesis gel (Janssen et al. 2003); (right) diagram illustrating the concentration profile of benzene (A), ethylene (B), and ethylbenzene (C) on a conventional zeolite crystal and a mesoporous zeolite prepared by the carbon templating process (Christensen et al. 2007).

Recently, Christensen et al. (2007) have investigated simultaneously the catalytic activity and diffusion rates of benzene and ethylbenzene in mesoporous ZSM-5 crystals. The catalytic tests show that for zeolites of nominally the same crystal size, the reaction rate for benzene alkylation is much faster for the mesoporous zeolite than for the conventional zeolite crystal. Using the classical ideas of diffusion-controlled transport in catalyst pellets, they derive activation energies for the diffusion of reactants and products. Their analysis indicates that the effect of the mesopores is to accelerate the transport of reagents into the crystal (and products out of the crystal). Their analysis provides an explanation for increases in both selectivity and activity for the reaction investigated.

Micro-Mesoporous Catalysts by Assembly of Nanoparticles

The group of Feng-Shou Xiao at Jilin University (see site report in Appendix C) has devised a still different approach (Li et al. 2005; Tang et al. 2007; Wang et al. 2005). In this case, the investigators first prepare a solution of zeolite precursor nanoparticles by mixing, for example, water, tetraethylorthosilicate, and tetrapropylammonium. This particular mixture, when heated to ~100°C for short periods of time, gives rise to nanoparticles that are a few nanometers in diameter. These nanoparticles are then put in contact with a mixture of surfactants: Pluronic P123 and $(C_3F_7O\text{-}C_3F_6O)_2CFCF_3CONH\ (CH_2)_3N^+(C_2H_5)_2$ and water. This mixture is stirred and heated under hydrothermal conditions at 180°C. The product contains a very well-defined mesoporous structure similar to the one of mesoporous silica USB-1. The composite material is called JLU-20 (Figure 2.6).

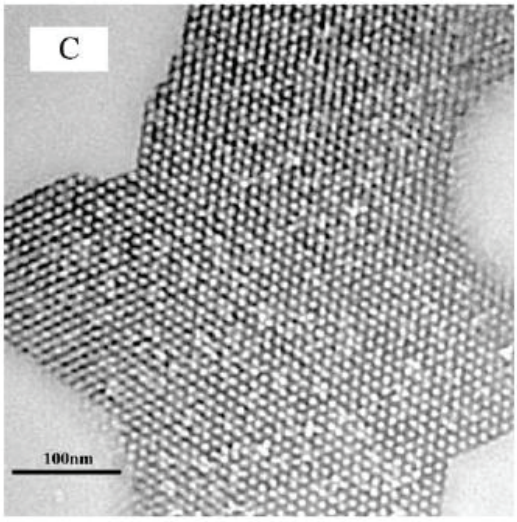


Figure 2.6. TEM image of JLU-20 showing the hexagonal arrangement of mesopores and the internal zeolite structure (Li et al. 2005).

Using a combination of nitrogen adsorption isotherms, nuclear magnetic resonance and infrared spectroscopy, and catalytic tests, the researchers at Jilin University show convincingly that the materials they prepare contain both mesoporosity and microporosity reminiscent of the properties of ZSM-5 crystals. Unfortunately, at this time there is no report describing the catalytic chemistry of the JLU-20 samples, and these cannot be compared to the two previous examples.

These three examples of mesoporous zeolites show the diversity of approaches that can be used to reach a common goal. Successful preparation of these complex materials depends on the self-assembly capabilities of the chosen nanomaterials as well as keen understanding by the researchers of both the aqueous chemistry of inorganic oxides and the colloidal chemistry of charged particles in an aqueous environment

SYNTHESIS OF EXTRA-LARGE-PORE ZEOLITE ITQ-33

The group of Avelino Corma at the Institute de Tecnología Química (ITQ) de Valencia (see site report, Appendix D) recently reported a new zeolite material with two important new structural characteristics (Corma et al. 2006). This material contains channels with 18-ring pores (Figure 2.7) ~12.5 Å in free diameter in one crystal direction, and in two perpendicular directions contains 10-ring (5.5 Å) channels. Prior to the synthesis of ITQ-33, several extra-large-pore zeolites (containing more than 12 rings as the minimum pore dimension) had been synthesized. In particular, ECR-34, a gallium silicate, contains one-dimensional pores of similar size to ITQ-33. However, ITQ-33 has pores in three dimensions, and it is prepared with a simple structure director, hexamethonium cations.

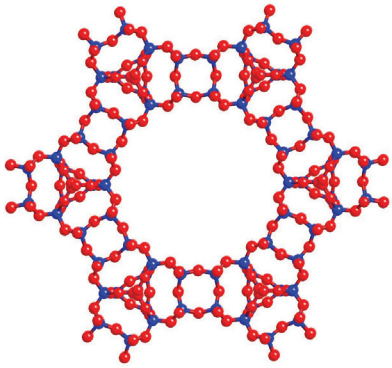
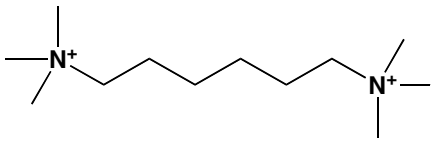


Figure 2.7. Structure of the new 18-ring zeolite ITQ-33.

The successful synthesis of ITQ-33 requires four ingredients. The first ingredient is a structure director (hexamethonium) that fills in the pore space not occupied by the silica framework. The second ingredient is the presence of some fluorine ions in the synthesis gel. These ions are incorporated in the as-synthesized material to balance (in part) the charge of the organic structure director and end up typically occluded in some of the small cages of the zeolite structure. In this form, the fluoride anion has both a stabilization effect for small cages and a structure-directing effect by selecting structures that have these cages. The third ingredient for the synthesis of ITQ-33 is the addition of some germanium oxide (in addition to silicon dioxide) to the synthesis gel. The larger Ge-O bond distances also stabilize cage structures that are different from the ones usually observed in pure silicates. The final crucial ingredient in the synthesis of ITQ-33 is the use of high-throughput synthesis methods. Originally, ITQ-33 was found as a small impurity in a set of exploratory synthesis compositions (Corma et al. 2006) investigated by the Spanish group. By the combination of statistical design of experiments and high-throughput experimentation, Corma and collaborators found narrow synthesis conditions that allow for the preparation of this material in pure form. It is especially interesting that a small and flexible organic molecule such as hexamethonium is capable of stabilizing such a large and open structure.



Scheme 2.3: Hexamethonium.

The catalytic tests conducted with this zeolite indicate that the acidity of ITQ-33 is of similar strength to that of acidity of other high-silica zeolites. For instance, in the alkylation of benzene with propene to make cumene, ITQ-33 gives high selectivity at high conversions (with less than 0.01% by-products at 99% conversion), and the rate of deactivation is slower than the rate of deactivation of comparable commercial catalysts such as zeolite beta. ITQ-33 has also been tested for the cracking of vacuum oil, where it has shown several important qualities. First, it gives a conversion higher than zeolite beta and similar to zeolite USY.

Second, it gives higher diesel selectivity without loss of the yield of butanes and propene. Because ITQ-33 can be prepared using a simple and inexpensive organic structure director, and because it has unique catalytic properties while maintaining good stability, it is quite possible that this rather exotic material will find industrial applications. This material is very new, and much can be expected from further study of its catalytic properties.

HETEROPOLYANIONS AS PRECURSORS FOR DESULFURIZATION CATALYSTS

Hydrodesulfurization is a very important catalytic process used to remove sulfur from oil feedstocks by the selective hydrogenation of carbon-sulfur bonds. The catalysts are usually prepared by impregnation of γ–alumina with ammonium heptamolybdate and cobalt nitrate. This precursor material is sulfided to yield MoS_2 crystallites (a layered material) with cobalt atoms decorating the edges of the layers. It has been found empirically that a Co/Mo ratio of 0.5 gives the most active catalysts.

In order to improve over the existing catalysts, IFP and the Catalysis Laboratory at Lille in France (Martin et al. 2005; Mazurelle et al. 2008) have developed a new route to the preparation of hydrodesulfurization catalysts based on heteropolyanions (HPA) of molybdenum and cobalt. The basic idea is to use HPA with atomically mixed Co and Mo as a way to enhance the formation of small crystallites upon sulfidation. The starting point was the Anderson HPA of composition $CoMo_6O_{24}H_6(NH_4)_3$. Since the ratio of Co/Mo is below the optimal value, IFP and the Lamonier laboratory developed a synthesis of the dimer of this HPA $(Co_2Mo_{10}O_{38}H_4)^{6-}$ and then exchanged the ammonium form with cobalt to form a compound with the desired Co/Mo ratio.

Generally, the researchers found that the use of simple HPA (with a Co/Mo ratio different from the optimal) already showed improved activity over the materials prepared with heptamolybdate and cobalt nitrate. The new Co-exchanged Anderson HPA dimer resulted in even better activity than all previous samples. The origin of this enhanced activity can be explained based on TEM images of the standard catalysts and of the HPA-catalyst (Figure 2.8). The images show that the use of the HPA reduces the effective size (diameter) of the MoS_2 layers, generating more active sites per unit mass of catalyst. In the figure, disordered individual layers of the MoS_2 are the most commonly observed structure on the HPA-based catalysts. On the traditional catalysts, the MoS_2 layers are more organized in stacks of crystals, and in fact, the MoS_2 single layers can be observed to surround some of the alumina particles. The structure of the traditional catalysts leads to low levels of layer edges, the place where the active site of the catalysts is believed to be located.

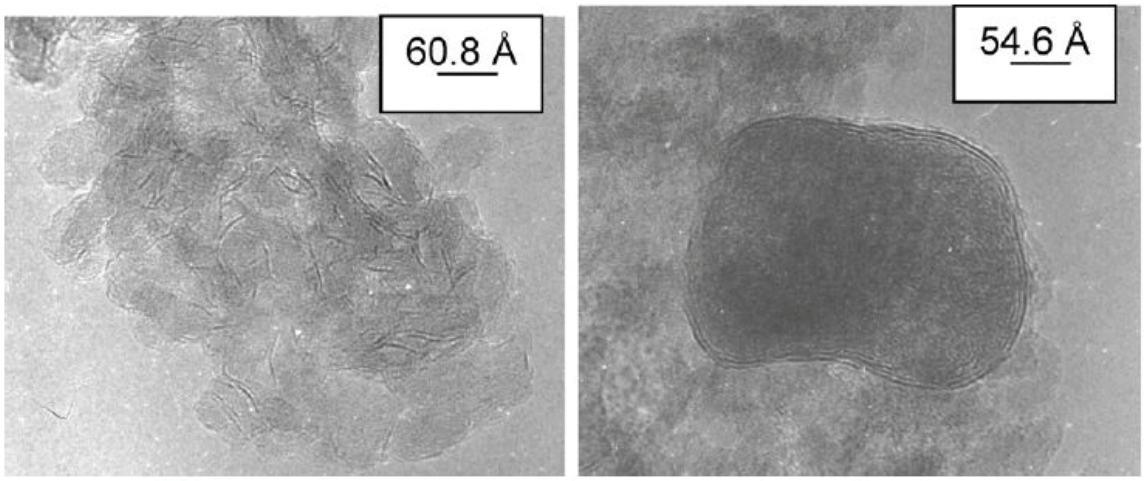


Figure 2.8. TEM images of sulfided HDS catalysts prepared using an Anderson dimer HPA (left), and conventional ammonium heptamolybdate, and cobalt nitrate (right) (Lamonier et al. 2007).

FINAL REMARKS

This chapter has described recent international advances in the synthesis of nanostructured catalysts that have shown promise to improve upon the activity or selectivity of existing catalysts. Multiple times in visits to labs in Europe and Asia, WTEC panelists observed the use of preformed nanostructures as starting blocks upon which the final structure is formed or developed. Panelists also observed that the characterization techniques developed for the nanotechnology revolution have been extremely helpful to the characterization of novel catalysts with nanostructures and have promoted an intensification of efforts across the world to improve important catalysts already in use or under development.

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CHAPTER 3

SPECTROSCOPIC CHARACTERIZATION OF NANOSTRUCTURED CATALYSTS

Jeffrey T. Miller

BACKGROUND

Much of the productivity improvements in the chemical industry within the last century could not have occurred without the help of catalysts. Catalytic materials provide improvements in reaction rate and product selectivity by lowering the activation energy by which chemical reactions occur. A wide variety of chemical substances show catalytic activity, however, most industrial processes employ heterogeneous catalysts that are comprised of metal, metal oxide, or metal sulfide nanosized particles on porous, high surface area supports. Additionally, some microporous and mesoporous catalysts have acidic properties. Three characteristics are common to every catalyst, e.g., activity, selectivity and stability. In order to optimize the catalyst efficiency, it is necessary to control the composition, physical properties and reactor environment. As a result, although the catalytic site may be of nanoscale size, characterization of the catalyst system requires methods that span the size range from atomic to nanometer to millimeter to meter length scales, Figure 3.1.

Figure 3.1. Characterization of nanoscale catalysts at different length scales. From left to right: tens of meters (commercial reactor), millimeter scale (catalyst extrudates), micron scale (particle morphology), and atomic and nanometer scale (nanoparticles in mesoporous support) (courtesy of B. Weckhuysen, Utrecht University, Netherlands).

In addition, as the nature of the catalytic phase is often altered by the reaction environment, i.e., reacting to gases, temperature, time, etc., it is necessary to make measurements under realistic operating conditions. Many of the instrumental methods do not operate under extreme operating conditions; nevertheless, it remains a central goal in the catalysis field to make precise measurements of the catalyst under working conditions. This chapter reviews recent developments in the characterization of nanoparticle catalysts with particular emphasis on *in situ* or *operando* methods. This chapter only covers spectroscopic methods. Microscopy and related imaging techniques are covered separately in Chapter 4.

LABORATORY CHARACTERIZATION METHODS

Overview

Spectroscopic characterization methods are relied upon at all stages of the catalytic process, from preparation, pretreatment, and reaction to post-process analysis. Modern laboratories typically utilize a number of commercially available instruments to obtain this preliminary information. Typically available techniques include gas chromatography, physisorption and chemisorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron spectroscopies (X-ray photo-electron [XPS] and Auger), and electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR) ultraviolet/visible (UV/Vis), Raman, and infrared (IR) spectroscopies. Across Asia (China, Korea, and Japan) and Western Europe, most researchers that the WTEC panel visited had a significant number of new instruments with the latest improvements. This was especially true in China, where funding for new equipment was very high. In addition, many of the top universities in Asia and Europe had several faculty (4–10) involved with catalysis research, which allowed them to purchase larger, more expensive equipment, e.g., NMR, TEM, etc., for catalyst research.

With a few exceptions, most catalytic scientists are not instrument design engineers; thus, they rely on commercial instrument manufacturers for continued improvements. While instrument capabilities are improving at a rapid rate, standard commercial designs often do not allow for measurement under reaction conditions. As a result, catalytic scientists adapt existing equipment and develop controlled atmosphere reaction cells for *in situ* measurements. At many institutions in Europe, there are permanent staff scientists who maintain, operate, and modify equipment for the research scientists and graduate students. With years of experience, these highly skilled staff members are able to design special equipment and conduct difficult experiments necessary for the most in-depth and sophisticated analyses. In addition, these personnel provide the institution the continuity of skills necessary to more rapidly advance equipment development. In contrast, in the United States, once graduate students obtain their degrees and leave the labs, often critical skills are lost or must be relearned by the next generation of students.

New Spectroscopic Capabilities and Adaptations to Standard Laboratory Instruments

In Situ UV/Vis Spectroscopy for Zeolites

Zeolites are crystalline, solid acid catalysts used for a variety of reactions. For large crystals, electron and optical microscopy show few internal details. UV/Vis spectroscopy can detect internal structure by detecting light-absorbing or -emitting hydrocarbons adsorbed in these zeolites (Karwacki et al. 2007). Using an *in situ* cell to control the temperature and hydrocarbon partial pressure, the spacially resolved, time-dependent reactivity of different size reactants can be determined (Kox, Stavitski, and Weckhuysen 2007). Additionally, a laser source can reveal complementary fluorescence spectra (Stavitski, Kox, and Weckhuysen 2007). These methods have also been used to map the distribution of Brønsted acid sites in zeolites.

Catalyst Preparation

Several new characterization techniques are being developed to follow the steps during catalyst preparation. In industry, catalyst preparation often involves the addition of a solution of metal salts to millimeter-sized pellets. Time-resolved Raman (Bergwerff et al. 2004; Bergwerff et al. 2005), UV/Vis/NIR (Water et al. 2005), and tomographic energy-dispersive (Beale et al. 2007) spectroscopies have been applied to follow the distribution and interaction of the metal salts on extrudates. Analysis of the Co and Mo addition to alumina, for example, shows that Co is uniformly distributed, Mo is distributed near the edge region, and there is a thicker edge region where a mixed Mo-Co complex deposits. In addition, there is a region near the center with low Mo concentration; thus, these analyses indicate an opportunity to better optimize the preparation for improved performance. Time-resolved Raman spectroscopy has also been used to observe the effect of metal ions in the synthesis of substituted aluminophosphate molecular sieves. Addition of Zn^{+2} ions, for example, alters the interaction between the gel and template, leading to a different template conformation and microporous structure (O'Brien et al. 2006).

In the absence of metal ions, hydroxyl groups on alumina, for example, can be detected by ^{1}H NMR, while the presence of metal ions quenches the signal. ^{1}H NMR imaging (MRI) has been developed to follow the distribution of metals on a single extrudate particle during impregnation (Bergwerff et al. 2007). Figure 3.2A shows the time-dependent impregnation of Co^{+2}-citrate complex on alumina at different times, and Figure 3.2B shows the different Co distributions that can be obtained by different preparation conditions. Depending on the catalyst application, one distribution will be more preferred than others.

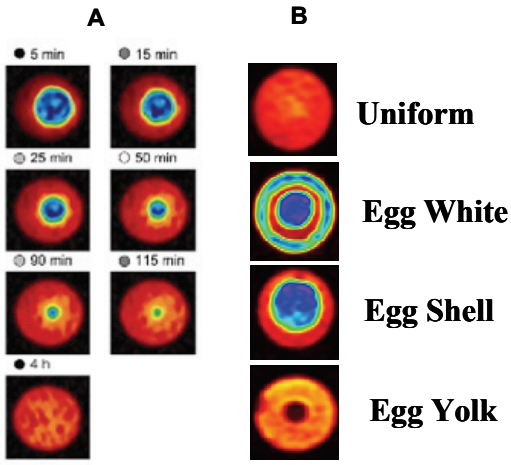

Figure 3.2. (A) MRI of Co-citrate on alumina at different times; red indicates region of Co ions. (B) Distribution of Co on alumina with different preparation conditions, e.g., pH, Co:citrate ratio, etc. (courtesy of B. Weckhuysen, Utrecht University, Netherlands).

Catalyst Surface-Adsorbate Spectroscopies

Critical to the understanding of any catalytic system are the structure, bonding, and electronic state of the active surface. Infrared and Raman spectroscopies have long been used to study the metal-adsorbate interaction at high temperatures in the gas phase.

Attenuated Total Reflectance Infrared Spectroscopy

Typically, IR spectroscopy is conducted in the gas phase, because high gas concentrations or liquids overwhelm the signal from the surface-adsorbed molecules. Using a transient Attenuated Total Reflectance (ATR) IR spectroscopy (Bürgi and Baiker 2006) with a specially designed IR cell (Figure 3.3), the species adsorbed on a thin oxide film supported on a flat IR reflecting surface can be determined in the liquid phase (Urakawa et al. 2003). ATR IR has also been applied to the study of supercritical CO_2 reactions, spectroscopy in flames, and spectroscopy in aqueous environments (Schneider et al. 2003).

Ultraviolet Raman Spectroscopy

Raman spectroscopy, with its high resolution and wide spectral range, has been applied with success on heterogeneous catalysts for determination of adsorbed species and structure of crystalline and non-crystalline oxide phases. Raman is an especially attractive technique, due to its ability to characterize catalysts under reacting conditions. For many reactions, however, the catalyst is quickly covered with coke, which has a large fluorescence signal that interferes with the Raman bands. Utilization of an ultraviolet (UV) laser can minimize the fluorescence interference (Stair 2002). The Dalian Institute of Chemical Physics has extensively used UV Raman spectroscopy to characterize the charge transfer of $p\pi$-$d\pi$ transitions from the metal ion to the oxide lattice in metal-containing microporous solids. This technique also can be used to identify and quantify the metal atoms in a zeolite structure (Li et al. 1999; Yu et al. 2000; Xiong et al 2000). During the synthesis of Fe-ZSM-5, incorporation of Fe into the molecular sieve structure is followed by UV Raman.

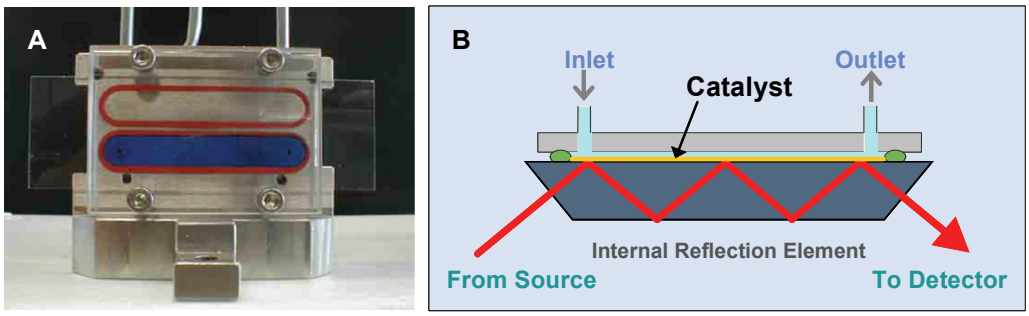

Figure 3.3. (A) ATR IR cell for liquids; (B) a schematic of the ATR sample showing a thin oxide supported on a flat substrate (courtesy of A. Baiker, ETH, Switzerland).

Spectroscopies for Catalytic Reactors

In situ UV/Vis and Raman spectroscopies have been used to quantify the amount of coke formed during reaction (Nijhuis et al. 2003; Tinnemans et al. 2005). Using multiple detection points along the bed length of a catalytic reactor (Figure 3.4), it is possible to determine the amount of coke at different locations (Bennici et al. 2007). During the reaction, the detectors monitor the buildup of coke, and at a predetermined level, the reaction is terminated and the catalyst is regenerated. Such detection and control systems may be applicable to larger industrial equipment.

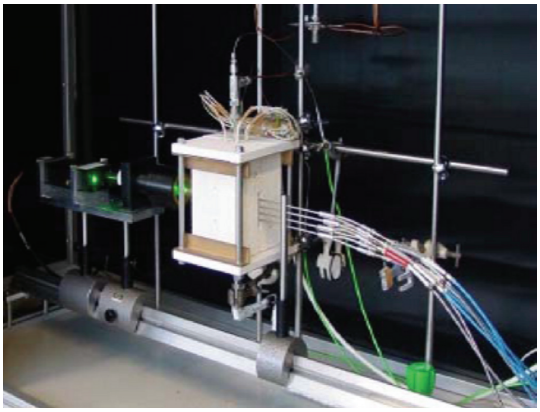

Figure 3.4. Catalytic reactor with multiple UV/Vis detectors along the length of the catalyst bed (inside the furnace); at the top of the furnace is a Raman detector (courtesy of B. Weckhuysen, Utrecht University, Netherlands).

Magnetic Resonance Imaging of Catalyst Beds

The advancement in magnetic resonance imaging (MRI) of catalyst systems is due in part to instrument advances, e.g., larger sample bores and more powerful magnets. The Magnetic Resonance Research Center at Cambridge University has the latest instruments and is developing exciting and novel applications for catalyst applications (and other fields). For example, using ^{13}C MRI, the concentration of reactants and products as a position in the reactor can be quantitatively determined during reaction. In addition, the deactivation of the catalyst bed and formation of coke can also be followed. Other applications include determination of heterogeneity in catalyst particles and determination of diffusion coefficients in catalyst pellets during hydrogenation reactions.

MRI has also been applied to other systems, including the flow patterns in ceramic honeycomb catalytic converters (Gladden 2003), the distribution of particles and voids in fluid beds as a function of gas rates (Figure 3.5), and liquid hold-up and wetting properties of liquid in trickle phase, fixed-bed reactors (Sederman and Gladden 2001). The latter has been applied in commercial reactors.

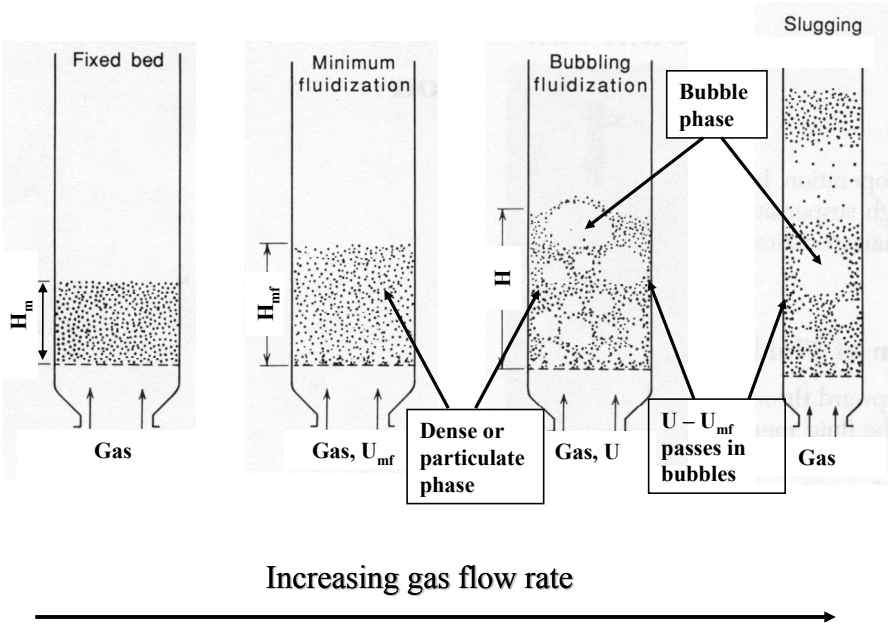

Figure 3.5. MRI of fluid bed nanoparticle catalyst and gas voids with increasing gas velocity (courtesy of L. Gladden, Cambridge University, UK).

New Instrument Development

While most institutions and scientists rely on instrument manufacturers for advances in instrumentation capabilities, there is a significant effort in the Department of Chemical Physics at the Fritz Haber Institute in Germany to continually push the limits of experimental techniques by developing new instrumentation. For example, the department is currently developing an ultrahigh-resolution spectromicroscope (known as SMART), low-temperature scanning tunneling microscopy (STM), and a high-field W-band electron paramagnetic resonance spectrometer, as shown in Figure 3.6.

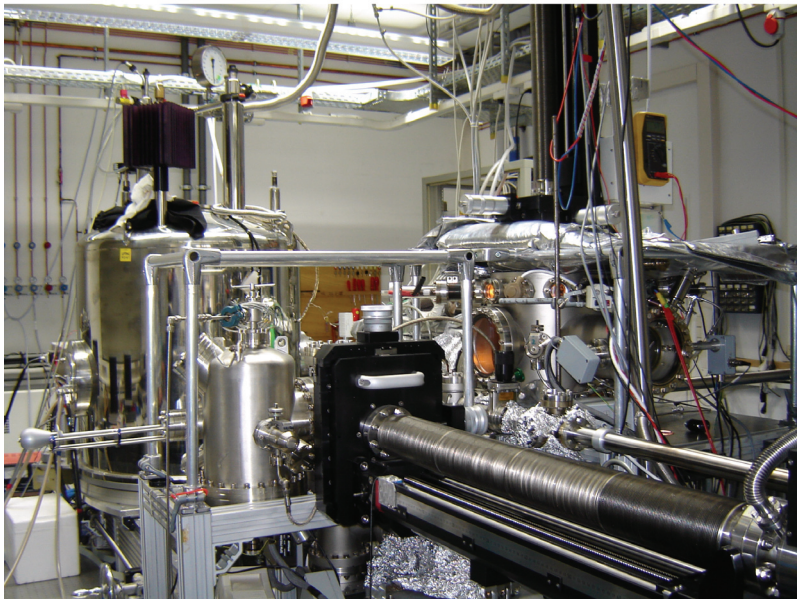

Figure 3.6. 95 GHz, ultrahigh-vacuum EPR spectrometer (courtesy of H. Freund, Fritz Haber Institute, Berlin, Germany).

SMART utilizes both chromatic and spherical aberration corrections to overcome the resolution limitations of currently available photoelectron emission microscopes (PEEM) to give lateral resolution of 2 nm and an energy resolution of 100 meV, which is claimed to be the most ambitious project in the field of spectroscopic microscopy in the world. In addition to performing photoemission spectroscopy, X-ray photoemission electron microscopy (XPEEM), and low-energy electron microscopy (LEEM), the tool can also be used for NEXAFS (near edge X-ray absorption fine structure), XPS (X-ray photoelectron), and Auger spectroscopy, as well as for diffraction methods such as micro-spot low energy electron diffraction (LEED) and photoelectron diffraction (PED). The ultrahigh-vacuum (UHV), 95 GHz, high-field EPR will improve the spectral resolution compared to state–of-the-art instruments and has been used to study bimetallic nanoparticle catalysts, paramagnetic centers in Ziegler-Natta catalysts, and paramagnetic reaction intermediates. By combining low-temperature STM with photon STM, the group hopes to record Auger spectra with nearly atomic resolution.

In addition to the impressive new capabilities under development at the Fritz Haber Institute Department of Chemical Physics, its Department of Inorganic Chemistry also has an impressive capability of more conventional analytical tools:

- Spectroscopic methods: Raman (5 wavelengths available), *in situ* UV/Vis/NIR (2 units), *in situ* IR (4 spectrometers with DRIFTS and transmission capability)
- *In situ* photoelectron and synchrotron radiation methods
- Chemical and physical tools: elemental analysis, *in situ* XRD, variable atmosphere differential scanning calorimetry (DSC), calorimetry (4 units), adsorption, temperature programmed desorption (TPD), temperature programmed reduction (TPR), TEM (3 microscopes), and SEM (2 microscopes)

SYNCHROTRON METHODS

Overview

The increase in the use of synchrotron techniques for characterization of catalysis is, in part, due to the increased availability of synchrotrons, as well as to improved data quality and improvements software for data analysis. In addition, because of the penetrating depth of X-rays, synchrotron techniques can be applied to catalysts under reaction conditions. The proliferation of synchrotron X-ray sources means that it is easier than ever to find a facility to do high-quality research.[3] In the last 15 years, three large new sources have been built for generating high-energy X-rays: the Super Photon Ring (SPring-8; Nishi Harima, Japan), the European Synchrotron Radiation Facility (ESRF; Grenoble, France), and the Advanced Photon Source (APS; Chicago, Illinois, USA), pictured in Figure 3.7.

Figure 3.7. Left to right: third-generation synchrotrons Super Photon Ring-8 (Japan), European Synchrotron Radiation Facility (France), and Advanced Photon Source (USA).

Existence of these newer, so-called third-generation sources with higher-power X-ray sources means that experiments can be performed in much less time, at much lower concentrations, and with increased signal-to-

[3] Current synchrotron facilities throughout the world are listed at http://www-als.lbl.gov/als/synchrotron_sources.html.

noise. Several new facilities are under construction or in the planning stage in the UK (Diamond), France (Soleil), and the People's Republic of China (Shanghai Synchrotron Radiation Facility, SSRF).

Scattering Techniques

X-ray diffraction has long been used for phase identification in heterogeneous catalysts, and with the high-intensity monochromatic light at synchrotron sources, diffraction patterns can be obtained in significantly shorter times. *In situ* X-ray diffraction patterns were obtained on a Pt on CeO_2-ZrO_2 auto exhaust catalyst in approximately 1 minute at the ESRF. By using a low dead-volume, *in situ*, capillary, plug-flow reactor with mass spectrometer to detect the reaction products, the catalyst performance was monitored as XRD results were obtained and the reaction temperature increased (Figure 3.8). CO was found to reduce the CeO_2, and the phase transition from tetragonal to monoclinic was determined with different gas compositions and reaction temperatures (Martorana 2003).

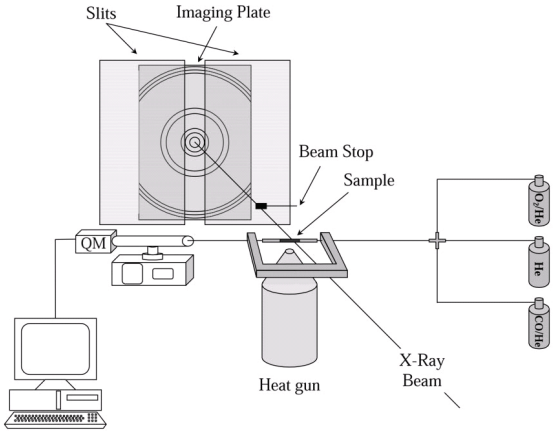

Figure 3.8. *In situ*, capillary XRD reactor at the ESRF (courtesy of R. Psaro, Institute for Nanostructured Materials, Palermo, Italy).

At the ESRF, time-resolved, *in situ* characterization of the synthesis of zinc-substituted microporous aluminophosphate was followed using multiple techniques, including small-angle X-ray scattering (SAXS), WAXS wide-angle X-ray scattering (WAXS), and XAFS. By combining these methods, the crystallization process could be simultaneously characterized at the molecular, nanoscopic and crystalline level (Fiddy et al. 1999). Figure 3.9 shows a schematic representation and a photo of the beamline.

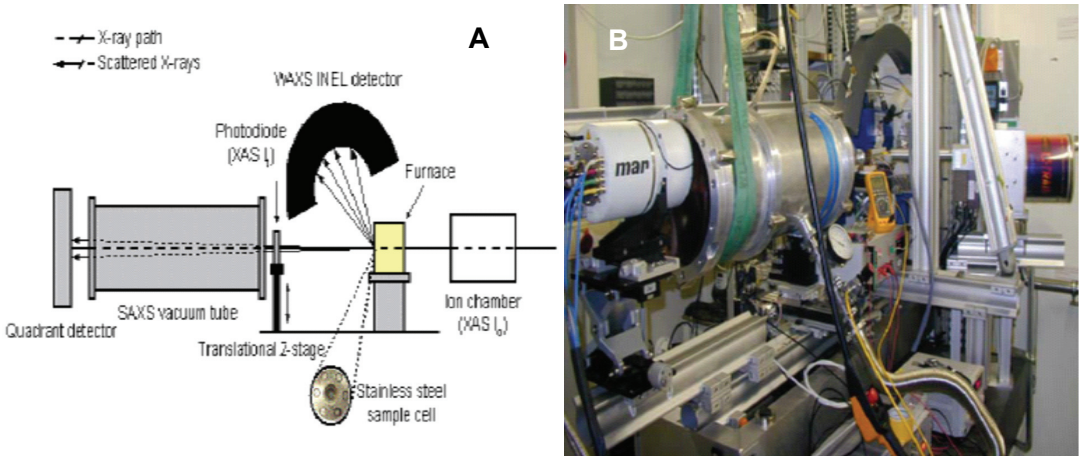

Figure 3.9. ESRF's beamline for simultaneous measurement of SAXS, WAXS, and EXAFS (courtesy of B. Weckhuysen, Utrecht University, Netherlands).

X-Ray Absorption Spectroscopy

Since many nanoscale catalytic materials lack long-range order or are sufficiently small to be undetectable by XRD, X-ray absorption spectroscopy (XAS) has become a widely used tool for structural (extended X-ray absorption fine structure, or EXAFS) and electronic (X-ray absorption near-edge structure, or XANES) characterizations. With the wider availability of higher-flux beamlines, EXAFS and XANES can be determined under reaction conditions to provide information on the active state of the catalyst. XAS characterizations also often provide complementary information to that determined by other methods.

With the high flux of the new, undulator beamlines at third-generation synchrotrons, data acquisition is significantly faster. Traditionally, spectra were taken by moving the monochrometer and collecting data for a few seconds, then moving to the next position. Such step-scan spectra typically took about one hour for a full spectrum. Additionally, at older facilities it was often necessary to average several spectra to have sufficient signal to noise to resolve subtle structural features. At new facilities with the higher flux, it is no longer necessary to stop the monochrometer to acquire data. In the continuous-scan or quick-EXAFS mode, data are obtained in a few minutes with excellent signal to noise. Step-scan spectra are now used for very dilute samples, although these may also be obtained in fluorescence. Very fast spectra can also be obtained by a dispersive EXAFS beamline design. With the dispersive EXAFS beamline, a bent crystal gives all energies at one time, allowing for very fast spectra acquisition. The ESRF (France) and Photon Factory (Japan) have dispersive EXAFS beamlines where spectra can be obtained in less than 0.1 sec (Figure 3.10).

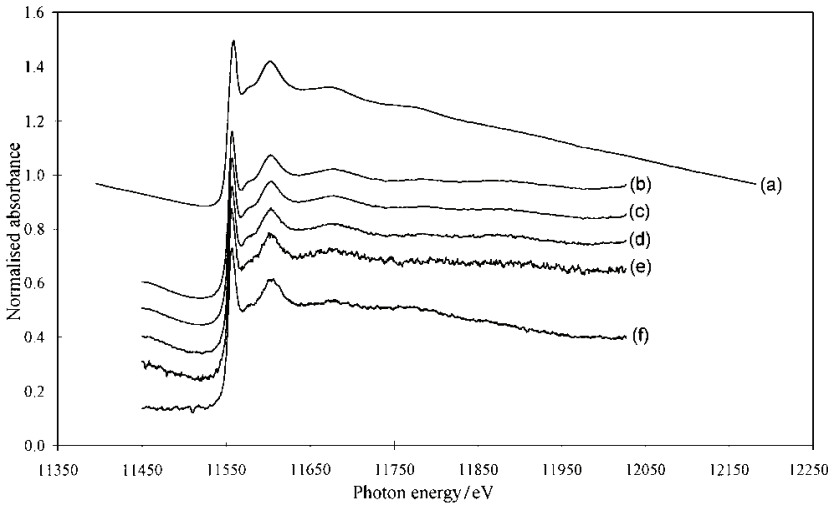

Figure 3.10. EXAFS spectra of 5% Pt on silica catalyst: (a) step-scan spectrum taken in 45 min.; (b–f) dispersive EXAFS, spectra taken at (b) 50 sec, (c) 5 sec, (d) 0.5 sec, (e) 0.05 sec., and (f) dispersive EXAFS spectrum of 1% Pt on silica taken in 21 sec. (Fiddy et al. 1999).

High-Energy Resolution XANES

XANES spectroscopy probes the local geometry and the oxidation state of the absorbing atom. XANES is also sensitive to adsorbates at the nanoparticle surface (Oudenhuijzen et al. 2005; Ramaker et al. 2003; Ramaker and Koningsberger 2002; Ankudinov et al. 2002). The intensity of the first feature in the L_3 edge spectrum reveals the number of holes in the d-band and, therefore, reflects charge transfer after adsorption of molecules. Fluorescence XANES, with an instrumental broadening below the core hole lifetime, greatly enhances the spectral resolution (Glatzel and Bergmann 2005; Hämäläinen et al. 1991; de Groot, Krish, and Vogel 2002; de Groot 2005). Figure 3.11A illustrates the enhancement in XANES resolution of Au foil measured in two modes: normal transmission (solid line) and high energy-resolution fluorescence (dotted line). A small white line is visible in the transmission spectrum while the XANES is enhanced in the high-energy resolution fluorescence spectrum. In addition, in the high-energy resolution spectrum, all other features are much more pronounced (van Bokhoven et al. 2006).

The XANES of an oxidized Au/Al_2O_3 catalyst shows increased white-line intensity consistent with partial oxidation of the Au surface. Figure 3.11B shows the evolution of the XANES spectra after switching to 1% CO. The spectra were recorded every 2 seconds and indicate that reduction is very fast, much faster than Au oxidation (van Bokhoven et al. 2006). In addition, upon reduction, small amounts of CO_2 are observed in the mass spectrometer, suggesting that catalytic site is an oxidized Au surface on the metallic particle.

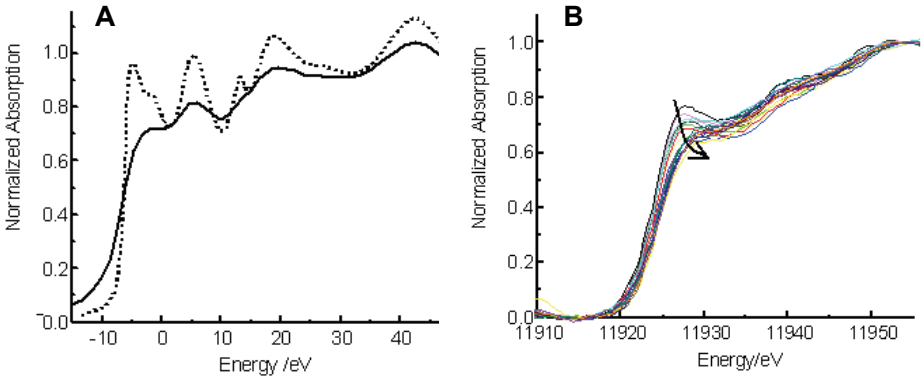

Figure 3.11. (A) XANES of Au foil: solid line = transmission; dotted line = high-energy fluorescence. (B.) Time-resolved (2 sec) XANES spectra of oxidized Au/alumina catalyst in 1% CO (van Bokhoven et al. 2006).

The increased sensitivity of the high-energy resolution fluorescence XANES combined with the *in situ*, time-resolved fast data acquisition provides a powerful new tool for quantitatively determining the kinetics of the elementary steps in the catalytic cycle. Coupled with the ability to simultaneously measure the reaction rate, it should be possible to determine how the catalyst composition (nanoparticle supports and modifiers) alter the kinetics of these elementary steps in the catalytic cycle.

Spacially Resolved XAS

XAS spectroscopy is typically a bulk technique, i.e., the spectrum is an average of all species that are present. However, during preparation and pretreatment, several phases may be produced. Thus, the EXAFS and XANES spectra may represent both the catalytic and non-catalytic species. XANES spectra of oxidized and reduced metals, however, occur at different energies and have different shapes. Therefore, the fraction of each in a partially reduced catalyst can be determined. With an *in situ* reaction cell designed to hold a single 600 nm Fe_2O_3 particle, the fraction of oxidized and reduced Fe during reduction and during Fischer-Tropsch reaction was determined by Fe XANES. Figure 3.12 shows the spatially resolved Fe L_{III} XANES spectra for the unreduced and reduced catalyst. The different colors represent different fractions of oxidized Fe (de Groot and Weckhuysen n.d.). Figure 3.12C shows the differences in XANES position and shape of the oxidized and reduced catalyst in one region of analysis.

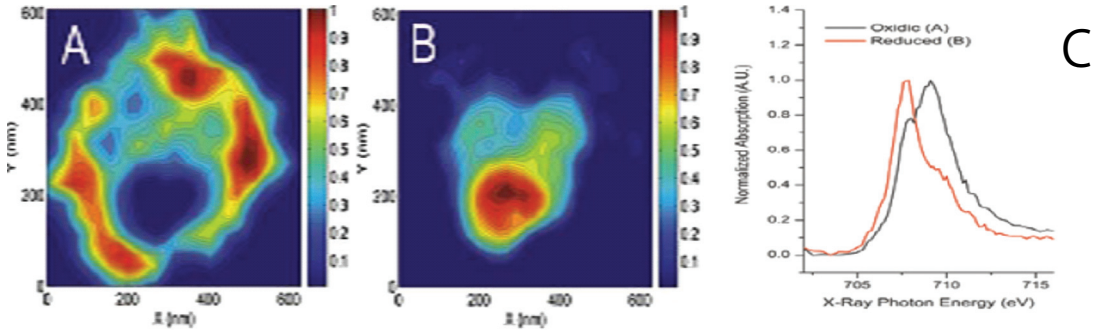

Figure 3.12. Spatially resolved XANES analysis of a single 600 nm Fe_2O_3 Fischer-Tropsch catalyst: (A) fresh, (B) reduced, (C) typical XANES spectra of a region of the catalyst before and after reduction (courtesy of F. de Groot, Utrecht University, Netherlands).

Millibar XPS at BESSY Synchrotron (Germany)

In a 10-year collaboration between M. Salmeron of the Lawrence Berkeley Laboratory, R. Schlögl of the Fritz Haber Institute, and personnel at the BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H., Germany) synchrotron, an *in situ* XPS beamline ("Innovative Station for *In Situ* Spectroscopy," or ISISS) was developed that could operate with pressures up to 10 mbar. The beamline exploits the synchrotron radiation of a bending magnet and is optimized to deliver photons in the energy range between 80eV and 2000eV with a high photon flux. It can be operated in different modes, that is, high flux, high spectral resolution, or higher order suppression (thereby increasing the spectral purity of the X-ray beam). The installation of a ventilation and safety system makes it feasible to use hazardous substances (e.g., flammable, explosive, or poisonous) as feed gas. In addition, ISISS is also equipped with a mass spectrometer to measure the reaction products while the spectrum is being obtained. A schematic of the high-pressure XPS and a photo of the experimental station are shown in Figure 3.13 (FHI n.d.).

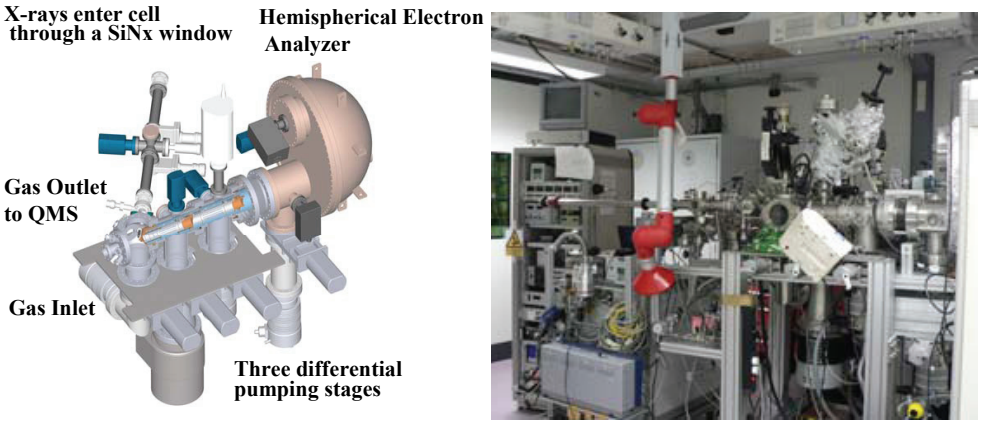

Figure 3.13. A schematic (left) and photo (right) of the HP-XPS at ISISS beamline at BESSY (Germany) (courtesy of Fritz Haber Institute).

The high-pressure XPS at BESSY has been used to study the oxygen species on Ru, Ag, and Cu. For example, subsurface oxygen was found in polycrystalline Cu foil during the partial oxidation of methanol to formaldehyde. The abundance of this species is correlated to the yield of formaldehyde, as Figure 3.14 shows.

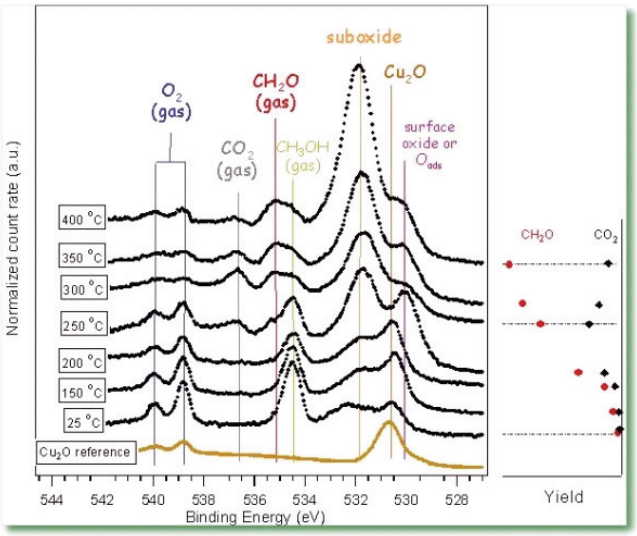

Figure 3.14. Photoemission spectra of a polycrystalline Cu foil under reaction condition: CH_3OH / O_2 = 3:1 and 0.4 mbar (Knop-Gericke n.d.).

CONCLUSIONS

In-depth, high-quality spectroscopic characterizations are essential for effective development of improved catalyst technology. New tools for understanding the structure, electronic properties, and adsorbed species of nanoscale catalysts under reaction conditions have progressed rapidly in the last decade. Today, there are many more methods to understand the catalytic processes than ever before. As new methods are reported, these are quickly adapted by other groups and applied to other materials. Often new approaches are also being adapted from other fields such as biology and physics. While there remains the need for higher resolution and quantification with many methods, improved instrumental capabilities will likely continue to come primarily from commercial instrument manufacturers and beamline design engineers at synchrotrons. The catalytic scientist will contribute to the advancement of these capabilities by working with these companies and synchrotron groups to define the needs of the field. For many laboratory instruments, these improved capabilities make the current generation of instruments obsolete in about ten years. Thus, it becomes important to replace aging equipment on a regular basis. New insights into new methods of preparation, materials, or catalytic phenomena cannot be discovered with outdated and ineffective tools.

Increasingly, more groups are making *in situ* catalyst measurements. While synchrotron research used to be limited to a few specialists who often wrote their own software for the analysis, today, access to modern, reliable synchrotrons is readily available, data quality is excellent, and user-friendly software is available. In addition, at many beamlines, equipment is available for conducting *in situ* experiments. With the level of detail that can be obtained with synchrotron techniques, the demand for these facilities is likely to continue to increase.

As the level of sophistication of spectroscopic methods increases, retaining skilled personnel to maintain these instruments and conduct difficult experiments becomes important. In organizations where there is no permanent staff support, once students graduate, expertise is lost and must be relearned; thus, the amount of time available for advancing the methodologies is reduced. At synchrotrons, most beamlines have staff scientists who assist with the experimental setup and execution of the experimental plan. They also maintain the beamline calibrating instruments, performing routine maintenance, and upgrading the equipment. Many universities in Europe have also recognized the value of permanent staff for operating multiuser instruments. They conduct instrument training, perform maintenance and upgrades, build sample cells, and assist new users with experiments. In addition to improving the quality of data and experiments, these staff scientists provide the continuity in expertise upon which further advancements can be built. This is a valuable practice.

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CHAPTER 4

ELECTRON AND TUNNELING MICROSCOPY OF NANOSTRUCTURED CATALYSTS

Renu Sharma

INTRODUCTION

The overall performance (that is, activity and selectivity) of catalysts is controlled by their size, morphology, nanostructure, and interaction with the support. Whereas nanometer-sized particles generally have higher reactivity due to their relatively high surface area, their morphology determines if they are bound by the active surfaces. For bimetallic, binary, and ternary oxide catalysts, the inter-granular and/or intra-granular heterogeneity in the sample may be a critical factor that determines their performance. Last but not least, since catalyst nanoparticles are generally supported on high-surface-area supports such as carbon, alumina, silica, or titania, we need to understand the interaction of the particle with the support, because the structure and morphology of the catalysts are strongly influenced by the nature of the support surface.

First and foremost the morphology, structure and chemistry of nanostructured catalysts are directly controlled by the synthesis. Therefore the ultimate goal of the characterization is to relate the synthesis methods to the structure and morphology and thereby to the activity and selectivity (performance) for heterogeneous catalysis at the nanoscale. Secondly, the temperature, pressure, and chemical environment often affect the morphology, structure and composition of the catalysts during operation, which may result in reduced activity, often known as catalyst poisoning. Therefore catalyst samples are characterized at various levels during synthesis and operation. Bulk characterization techniques, as described in Chapter 3, can often provide adequate information to achieve this goal. However, in order to understand atomic-level changes occurring during the synthesis and functioning of the catalyst, it is necessary to characterize them at high spatial (lateral) resolution. Therefore electron and tunneling microscopy techniques are often employed to determine the structural and chemical variations that exist in as-prepared or -used catalysts.

Overview of High-Resolution Characterization Techniques

Nanoscale characterization is employed for (a) general characterization of catalysts, and/or (b) to understand the changes occurring during the synthesis and/or functioning of catalysts. The latter is achieved either by characterization of materials before and after the reaction or by directly observing the dynamic process under reactive environments (*in situ*). There are several electron and tunneling microscopy techniques that can be successfully employed to obtain nanoscale information from individual catalyst and support particles. Following is a short description of some of these techniques.

Scanning Probe Microscopy (SPM)

Scanning probe microscopy (SPM) is a general term employed for microscopy techniques such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) that are used to form images of surfaces

using a physical probe that scans the specimen. In simple terms STM is based on the theory that when a conducting tip is brought near a metallic or semiconducting surface (within 0.3 to 1 nm distance), a current flow that is dependent on the local density of states is observed. The magnitude of this current depends upon the gap and the local barrier height. This current, also called tunneling current, represents the surface structure. Therefore, STM is very suitable for obtaining atomic-level structural and topographic information about the surfaces. Recent advances in instrumentation allow researchers to obtain atomic-level changes occurring on the catalyst surfaces in liquid or gaseous environments at different temperatures. Time- and temperature-resolved images are used to observe and understand the surface reconstruction and to identify surface adsorbates and chemical processes occurring during catalysis.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is widely employed to obtain topographic images and chemical information. In this case, as an electron beam (5–30 KeV) is used to scan the sample, a number of signals are generated, including secondary electrons, back-scattered electrons, and X-rays. Both secondary and back-scattered electrons are used to form images, and chemical information is obtained from the X-ray signals using energy-dispersive or wavelength-dispersive spectrometers (EDS or WDS, respectively). The spatial resolution for chemical analysis is dependent upon the probe size (electron gun and probe-forming optics) and can vary from a few nanometers to several hundred nanometers. Secondary electrons are emitted from the atoms occupying the sample surface and produce surface images, whereas backscattered electrons are produced by the reflection of the primary beam, and therefore their intensity depends upon the atomic number. The latter images are most suitable for locating heavy metal particles on light oxide surfaces. Environmental SEM (ESEM) with heating and cooling stages is often used to observe catalysts under working conditions. Recently, orientation image microscopy (OIM) has been incorporated with SEM and is used to obtain the preferred orientation of various particles and their relationship to the support.

Scanning/Transmission Electron Microscopy (STEM/TEM)

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and scanning-transmission electron microscopy (STEM) are more complicated and expensive techniques compared to STM and SEM. Here, high-energy (typically 100–1000KeV) electrons are used to obtain diffraction data and images from very thin (10–50 nm) samples. Figure 4.1 shows an HRTEM instrument (left) and a simple cross-section (right) of a TEM, including the modifications incorporated for observation of environmental effects, generally known as an environmental transmission electron microscope (ETEM). In the HRTEM, high-energy electrons (of short wavelength) generated by a field-emission gun (FEG) are focused on the sample by magnetic lenses (C1 and C2 in Figure 4.1). The electrons interact with the electron potential (density of states) of the atoms as they travel through the sample. An objective lens (OL), also known as an image-forming lens, is used to focus the transmitted and the diffracted beams to form diffraction-pattern and high-resolution images that are magnified and projected by another set of lenses. Some of the electrons lose energy as they interact with the sample and generate an X-ray signal (similar to SEM). Both the X-ray signal and the energy lost by electrons are characteristic of the electron potential in the sample and can be collected using suitable detectors, e.g., EDS and electron energy-loss spectra (EELS), to obtain local chemical information.

STEM images are formed by scanning the sample (similar to SEM) using a nanometer-size probe. By using suitable detectors, such as a high-angle annular dark-field (HAADF) detector, atomic-resolution images are collected, with intensity in the image directly proportional to the square of scattering power of the atoms (Z^2). HAADF images are most suitable for obtaining the size distribution of catalyst particles. Since most of catalyst particles are heavy metals (Au, Pt, Ni, Fe, Cu, MoS_2, etc.) supported on lightweight oxide supports such as silica and alumina, very-high-contrast images are obtained. Although HAADF images are not as easy to obtain as SEM or TEM images, particle size can be determined unambiguously, because the boundary of the particles is clearly marked due to the high contrast in the images. Moreover, because these images are usually obtained using very small probe size (0.2–0.5 nm), nanoscale chemical information, obtained using either EDS or EELS, can be combined with the images to obtain the chemical information from the regions around and within the catalyst particles. Therefore, STEM analysis is often employed to characterize nanoscale heterogeneity in the samples.

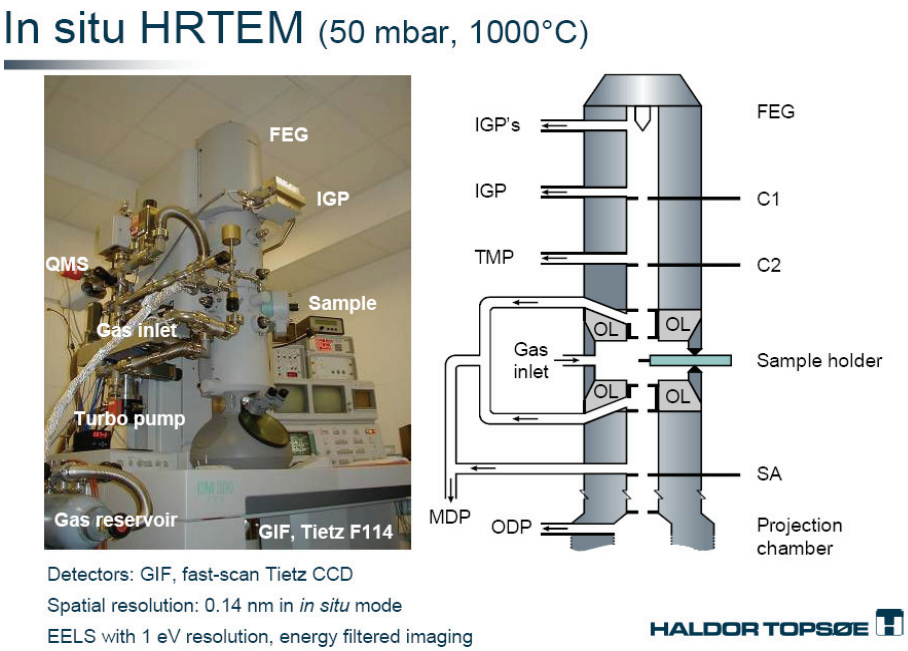

Figure 4.1. HRTEM instrument (left) and cross-section of the column (right) showing the electron source (labeled FEG), condenser lenses (C1 and C2), objective lenses (OL), location of sample, and projection chamber where the image is formed. Components of the modification made to introduce gases in the sample chamber area (gas inlet), and the differential pumping systems (MDP, ODP, and IGP) are also shown (courtesy of Haldor Topsøe).

In order to observe atomic-level structural and chemical changes, the TEM column can be modified to incorporate a gas inlet system and differential pumping apertures to constrain reactive gases in the sample area (Figure 4.1, right). With careful design, the rest of the column can be kept at high vacuum while the sample area can be at up to 50 mbar gas pressure. Suitable sample heating holders are used to observe the dynamic evolution of nanostructures and chemical changes at the atomic scale in gaseous environments at elevated temperatures (900–1000°C). Both TEM and STEM images can be obtained using an ETEM (Gai 1999; Sharma 2005).

Low Energy Electron Microscopy (LEEM)

As the name implies, low-energy electron microscopy (LEEM) uses very-low-energy electrons (0–100eV) to form images based on the diffraction and phase of the sample. It is a surface characterization technique, because these electrons do not have enough energy to penetrate through the sample. The image formation does not require scanning; therefore, it is fast and often used to observe time-resolved changes.

Photo Emission Electron Microscopy (PEEM)

In the original photo emission electron microscope, the photons from UV light incident on the sample were used to form images but now other light sources are also being used. The principle of image formation is that the photoelectron emission is produced if the energy of the incident photons on a sample is larger than its work function. An electron-optical imaging system is used to extract the photo-emitted electrons by a large electric field that is applied between the sample and the first electrode of the electron optical system. A combination of several such systems is used to obtain a full-field image of the emitted electrons onto a detector such as a phosphor that converts electrons into visible light. Several other photon sources, such as X-rays, are currently being used to form images that can also provide chemical information.

WTEC panelists found that SPM, SEM, and STEM/TEM are the techniques most commonly employed in the various laboratories we visited in Asia and Europe. Therefore, this chapter focuses on those techniques only.

GENERAL CHARACTERIZATION OF CATALYST PARTICLES

Particle size, shape, and composition (in the case of bimetallic or mixed oxide catalysts) can be determined using STM, SEM, TEM, and/or STEM. These techniques provide information at various levels of image, spatial, and temporal resolution. SEM is often employed to quickly scan the samples synthesized under different conditions or using different methods. The general information about the particle size distribution and chemical composition of individual particles thus obtained is then used to optimize the synthesis process for a specific application.

An example is the characterization of titania (TiO_2), which is an important photocatalyst with applications ranging from water purification to synthesis of hydrogen by water splitting as well as a catalyst support material. It has been shown that catalytic properties of TiO_2 can be improved by changing its morphology. Its photocatalytic activity is limited by the band gap (3.0–3.2 eV for anatase). Prof. Centi (University of Messina, Italy, and member of the EU Integrated Design of Catalytic Nanomaterials consortium) has shown that ordered helical structures (Figure 4.2) produced by the anodization of titanium foils have improved properties in the UV-visible region. Titania nanostructured thin films (TNT) were observed to have a linear relationship between wall thickness and the band gap. SEM images (Figure 4.2) were used to optimize the synthesis methods that will produce the TNTs with desired morphology and thereby improved properties (Perathoner et al. 2007).

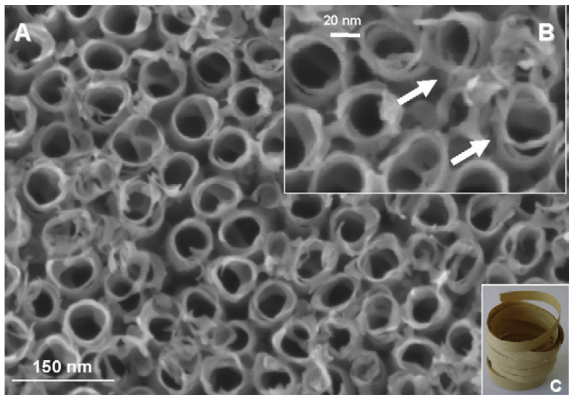

Figure 4.2. Field-emission SEM image of the sample obtained by anodization at 15 V for 45 minutes. In the inset (B), an expansion of some TNT shows the nanostructure of a helical nanocoil. In the inset (C), a photo of a rolled paper streamer is reported as an example to better illustrate the nanostructure (Perathoner et al. 2007).

Particle size is another crucial parameter for catalytic activity, especially for Au catalysts. Au is normally an inert material, but in 1995 Hutchings and colleagues at Cardiff University in the UK (see site report in Appendix D) showed that nanostructured Au particles with less than 55 atoms are the most active catalyst for a higher alkene epoxidation reaction; however, due to the high mobility of Au atoms, it is difficult to synthesize and control their size on a support (Hughes et al. 2005). Dr. Lambert's group at Cambridge University (see site report in Appendix D) has synthesized Au nanoparticles on various supports using cluster chemistry. TEM analysis of supported and unsupported Au particles with various loadings showed that both loading and support control the particle size (Figure 4.3). Higher selectivity of styrene oxidation was achieved using small particles ($\approx$1.5 nm), obtained with 0.6% loading on boron nitride (BN) and silica (SiO_2) and conversion rates of 19.2% and 25.8%, respectively.

Hydrogen peroxide (H_2O_2) is a key chemical commodity with numerous applications; its direct synthesis is one of the most challenging targets for the control of reaction selectivity in heterogeneous catalysis. A major breakthrough for direct synthesis was obtained using an Au catalyst (Hughes et al. 2005; Enache et al. 2006). Later, a comparative study of the synthesis of H_2O_2 using 5% loading of Au, Au/Pd (4+1% and 2.5+2.5%), and Pd on TiO_2 showed that maximum productivity is obtained with Au-Pd catalyst (equal amounts Au and Pd)

(Hutchings 2007). Using STEM imaging combined with nanoscale EDS, detailed analysis of the individual particles in the most reactive samples (Figure 4.4) showed that particles consist of a Pd layer surrounding an Au core (core-shell structure). It was concluded that Au acts as an electronic promoter for the Pd-rich surface.

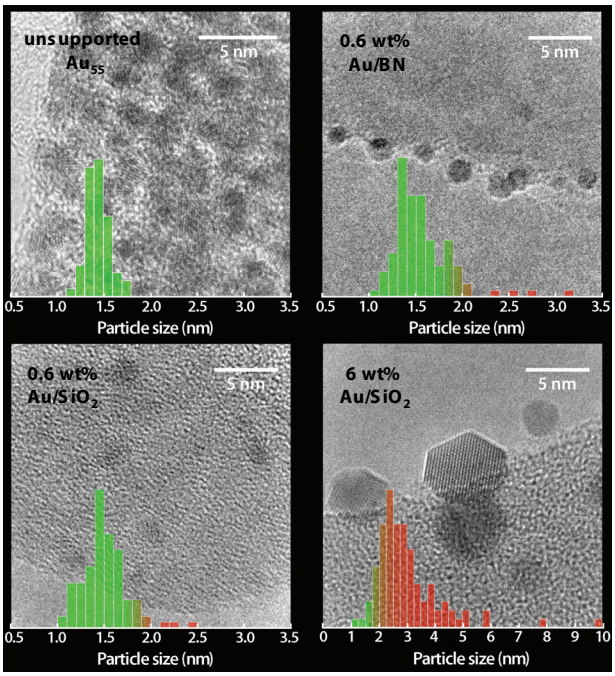

Figure 4.3. TEM images showing the size distribution of Au nanoparticles synthesized on different supports with various loadings (courtesy of Prof. Owain Vaughan, University of Cambridge, UK).

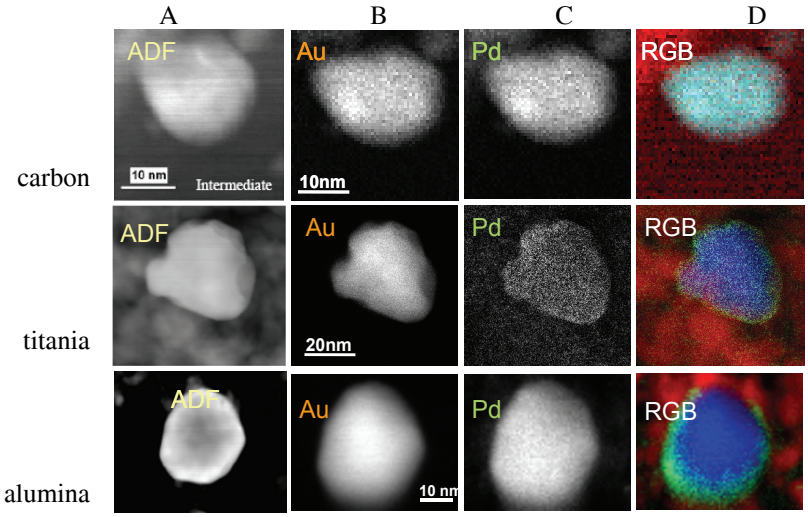

Figure 4.4. STEM-ADF (annular dark-field) image of 2.5 wt% Au–2.5 wt% Pd/TiO_2 catalyst calcined at 400°C, showing (A) large-alloy particles, (B) Au-M_2 STEM-XEDS (X-ray energy-dispersive spectroscopy) maps, and (C) Pd L_1 STEM-EDS maps. Note that the Pd signal appears to originate from a larger area than that of the Au signal, as demonstrated in the STEM. In column D, grey-level intensities from Au, Pd, and Ti are converted into colors (blue, green, and red, respectively), and their composite images show their distribution in individual particles on carbon (top row), titania (middle row), and alumina (bottom row) (courtesy of Prof. Graham Hutchings, Cardiff University, UK).

These examples illustrate the need for nanoscale characterization of both catalyst and support to understand and improve the activity and selectivity of nanostructured catalysts. For example, photocatalytic properties of TiO_2 are improved by changing the shape of the film (Figure 4.2); on the other hand, controlled synthesis results in nanometer-sized Au particles with improved properties. The activity of Au-Pd catalyst depends on the nanoscale composition and particles with a Pd layer surrounding an Au core giving maximum productivity.

NANOSTRUCTURE CHARACTERIZATION UNDER WORKING CONDITIONS

Ideally, catalysts should not change during a chemical reaction or should return to the same state between reaction cycles. However, both temperature and the nature of the gas/liquid environment often affect the morphology, structure, chemistry, and metal-support interactions during catalytic processes. Sometimes these changes are irreversible and restrict the long-term use of the catalyst. The reactive environment during synthesis also controls catalyst structure and morphology. Therefore, understanding the synthesis mechanisms that lead to high activity and selectivity of the catalysts as well as their functioning is a fundamental step forward to improve catalytic processes. The best way to understand the relationship of a nanostructured catalyst with its synthesis and its functioning is to follow the atomic-level changes occurring during synthesis and in a reactor, respectively.

Microscopy techniques are currently being used to study atomic- and near-atomic-level changes in two ways: (1) by characterizing the samples before and after the reaction, and (2) by making dynamic observations during the synthesis or operation of the catalyst. Regular STM, SEM, TEM, and STEM can be used for the first method, whereas special modifications are required for the dynamic imaging. Several examples are given below.

Effect of Environment on Surface Structure and Reactivity

Most catalytic reactions happen on surfaces; therefore, understanding the structure and chemistry of surfaces is an important part of the characterization. It has been shown that although CO does not adsorb on a clean Au {111} surface at 120 K and 5 x 10^{-8} mbar, it readily adsorbs under the same conditions if the surface has been pre-exposed to NO_2 (Zhang et al. 2005). Prof. King's group at Cambridge University (as presented by Dr. Driver in the WTEC panel's visit; see site report in Appendix D) has employed a combination of techniques such as reflection-absorption infrared spectroscopy (RAIRS), temperature-programmed desorption (TPD), LEED, and STM to understand the mechanism of surface activation as well as CO adsorption (Figure 4.5).

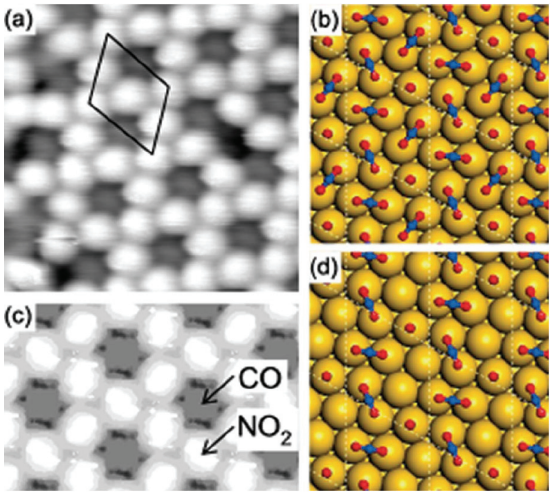

Figure 4.5. (a) STM image (28 x 28 $Å^2$, gray-scale range 1.5 Å, sample bias +0.10 V, current 1.0 nA) of an NO_2 +CO co-adsorbed layer, corresponding to the 3:1 structure shown in (b); (c) corresponding DFT Tersoff-Hamann simulation; (d) 2:1 model, for comparison (Zhang et al. 2005).

STM images (Figure 4.5a and c) show that a ($\sqrt{7}$ x $\sqrt{7}$)R19° surface reconstruction occurs due to interaction of the two co-adsorbed molecules (NO_2+CO). Density functional theory calculations for various NO_2-to-CO ratios revealed that the structure model for a 3:1 ratio matches the images obtained (Figure 4.5b), but other ratios do not (e.g., the 2:1 model shown in Figure 4.5d). These results also show that co-adsorption of electronegative species on coinage metals can be advantageous, contrary to the belief that adsorption of one electronegative species may poison the catalyst for the adsorption of other electronegative species.

Sintering

Nanostructured catalyst particles are often subjected to reactive gaseous environments at elevated temperatures, both during synthesis and under operations. Catalyst particles can sinter under these conditions, which results in the reduction of the surface area and thereby activity. Therefore, in order to eliminate or reduce the sintering process, it is necessary to determine its mechanism and the effects of reaction conditions on the process. Generally, sintering can occur in two ways: (1) particles become mobile on the support surface and coalesce upon contacting another particle, and/or (2) smaller particles become unstable due to high surface energy (Gibbs-Thompson effect); atoms from the smaller particles diffuse to larger particles via either surface or vapor diffusion, depending upon the temperature and their melting point. The latter process is also known as Ostwald ripening, where smaller particles continuously reduce in size and finally disappear while larger particles continue to grow. Dynamic observations at various temperatures have been employed to understand the sintering behavior. Both of these processes have been observed and have been found to depend upon the particle morphology, support, and temperature.

For example, STM images of a Pd layer deposited by chemical vapor deposition (CVD) on a titania {110} surface were recorded during heating to follow the sintering mechanism, as illustrated in Figure 4.6 (Bowker 2007). The images were recorded after the Pd layer was given ample time to achieve a stable temperature. It is clear from the images that de-wetting of the film resulted in the nucleation and growth of nanometer-size particles between 373 and 673 K, but the density of particles did not change considerably. However, particle size increased and density of particles decreased considerably as the temperature was increased from 673 K to 973 K. From these observations it is concluded that Pd particles do not sinter easily, and the fact that sintering happened only after 700 K indicates that it happened via the Ostwald ripening process rather than coalescence.

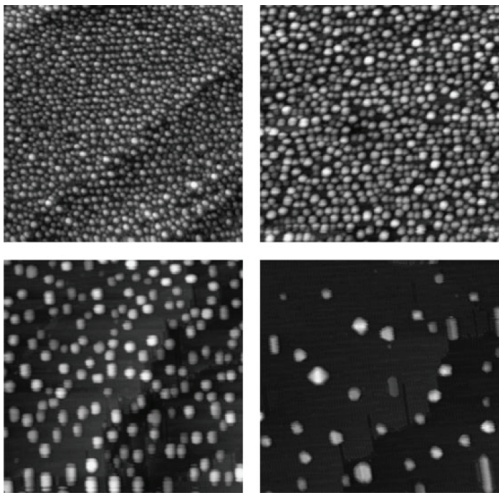

Figure 4.6. A series of STM images showing sintering of an array of Pd nanoparticles after heating the layer deposited at room temperature to 973 K. The image size is 100 x 100 nm. The images were recorded after the temperature was stable over long periods of time. Temperatures of the images were (top left) annealed to 373 K; (top right) annealed to 673 K; (bottom left) annealed to 873 K; and (bottom right) annealed to 973 K. Note that sintering only becomes marked above $\approx$700 K (Bowker 2006).

On the other hand, Dr. Kamino of Hitachi High-Technologies Corp., Japan (see site report in Appendix C), showed time-resolved (30 frames per second) videos of Pd and Au particles moving on the support surface at 693 K in 1.1×10^{-2} Pa of air and coalescing upon coming in physical contact with each other. It appears that the mobility of particles on the support controls the coalescence process, while atomic-scale diffusion results in Ostwald ripening.

Liu et al. (2005) have shown that the sintering can proceed by either of the two mechanisms on the same catalyst support system, depending upon the morphology. Pd/Al_2O_3 is widely used as industrial catalyst/support system for selective hydrogenation of acetylene. Reactivity of the catalyst has been observed to drop with time due to coke deposition on the catalyst surface. Heating at low temperatures (below 500°C) in steam is used to regenerate the catalyst. But the activity of the regenerated catalyst was always observed to be lower than that of fresh catalyst due to reduction in surface area. Direct observations of the sintering process were made using an environmental TEM (ETEM, Figure 4.1). *In situ* measurements showed that for fresh catalyst particles, significant sintering occurred only above 600°C by Ostwald ripening. On the other hand, sintering by coalescence was observed during the regeneration of used catalysts in steam at 500°C. As expected, used catalyst particles and support were covered with amorphous carbon that oxidized during heating in steam, and clean Pd particles became mobile on the support surface due to reduced metal-support interaction. Time-resolved (30 frames per second) observation showed that Pd particles move freely as the carbon coating burns out and coalesce when they come in contact with other particles. In fact, these regenerated particles were observed to catalyze the removal of carbon from the support surface, leaving channels for other particles to move freely and coalesce (Liu et al. 2005).

These observations show that the sintering process may be controlled by metal support interaction, morphology, temperature, and the natural gaseous/liquid environment. In order to maintain the activity and selectivity of the catalyst nanostructure, it is necessary to prevent an increase in particle size as well as any change in the structure of the exposed surfaces. Direct observations as described above can assist researchers in understanding the process and finding means to control particle growth.

Oxygen Spillover

STM is the most suitable tool to obtain atomic-level images of surfaces, but the microscope tip can itself enhance the surface reaction process. Somorjai and colleagues (McIntyre, Salmeron, and Somorjai 1994) have shown enhanced activity for the hydrogenation reaction as the STM tip scanned the surface of Pt catalyst, due to hydrogen spillover in its vicinity. Bowker and colleagues presented *in situ* images of oxygen spillover for 4 nm Pd nanostructures on TiO_2 (110) surface (Figure 4.7) (Bennett, Stone, and Bowker 1999).

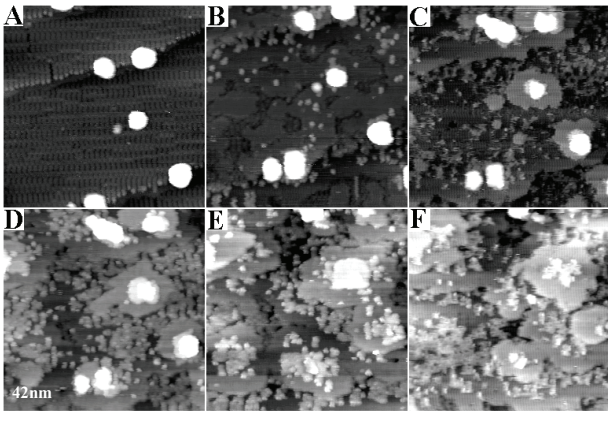

Figure 4.7. A sequence of images showing the reaction of oxygen with Pd nanoparticles on TiO_2 (110) at 673 K. Image size is 42 x 42 nm (A) is before reaction, and (B–F) is a sequence after exposure to a low-pressure stream of oxygen. The oxygen adsorbs at the Pd, and spillover to the adjacent titania then occurs (seen most clearly in C). The spillover oxygen grows new titania layers close to the particle much faster than elsewhere on the surface (Bowker 2007).

Time-resolved images recorded at 673 K in an oxygen atmosphere show that the oxidation reaction started in the region surrounding the catalyst particle. Oxygen molecules adsorbed on Pd particles dissociate more readily than on an oxide surface to form atomic oxygen, which is more reactive. Oxygen atoms are then carried by the STM tip and deposited in the vicinity of catalyst particles (spillover), forming new layers of titania close to the catalyst particle—observed as a bright ring around the particle (Figure 4.7C) that grew with time (Figure 4.7 D–F)—resulting in an ≈ 20-fold increase in reaction rate.

Synthesis of Catalyst Particles

Chapter 2 shows that there are various techniques currently employed for the production of nanostructured catalysts, and these synthesis methods control morphology, structure, and chemistry. Atomic-level variations in the structure and composition can have a huge impact on the life and performance of the catalyst; therefore, synthesis conditions must be optimized to produce nanostructures with desirable activity and selectivity. It is quite common to employ electron and tunneling microscopy techniques to characterize the catalyst nanoparticles produced by various synthesis techniques and use the knowledge obtained to select the synthesis method. For example, impregnation of inorganic salt solution is often used to synthesize metal oxide (after calcinations) or metal (after reduction) on high-surface-area supports such as silica or alumina.

Prof. de Jong's group at Utrecht University in The Netherlands (see site report, Appendix D) has used high-angle annular dark-field images to determine the size and location of NiO on SBA-15 nanoporous support (Figure 4.8), using different calcination routes to form NiO from decomposition of an aqueous solution of $Ni(NO_3)_2(OH)_4$. They found that calcination in flowing, compared to stagnant, air at 450°C reduced the particle size from 20–100 nm to 10–35 nm; the number and size of particles formed were observed to reduce further to 11–26 nm by replacing air with He. The most interesting result was that a uniform distribution of 4±1 nm-sized particles was obtained by adding 1% NO to the He flow during calcination. They also used electron tomography to show that most of the particles were located inside the pores of the SBA-15 support (Friedrich et al. 2007).

Researchers at Haldor Topsøe A/S in Denmark (see site report, Appendix D) have used *in situ* observations to understand the effect of environment on the surface structure and morphology of a catalyst during calcination. They have employed ETEM to observe dynamic evolution of nanostructure at the atomic scale. Cu/ZnO is the catalyst system employed for industrial production of methanol and is considered to be a promising catalyst for the conversion of hydrocarbons in fuel cell applications. The nature of the dynamic changes occurring with the change in the reducing gas composition under reaction conditions was determined using the ETEM (Hansen et al. 2002).

Figure 4.9 shows atomic-scale evolution of catalyst particles in nonwetting (Figure 4.9A and C) and wetting (Figure 4.9E) catalyst morphology that exposed different surfaces as the reduction environment was changed by adding water or CO to hydrogen. The particle shape and surface structure was observed to change back to the original form as H_2O (less reducing) or CO (more reducing) was removed from the hydrogen flow, confirming the reversible nature of the restructuring phenomenon. Wulff constructions (Figure 4.9B, D, and F) show the availability of low index surfaces, such as 111, 110, and 100, and absence of high index surfaces. The surface free energy calculated from these images depends on the contact angle. For example, the surface energy of all low index surfaces was found to be lowest for particle morphology obtained in H_2/H_2O gas mixtures (Figure 4.9B).

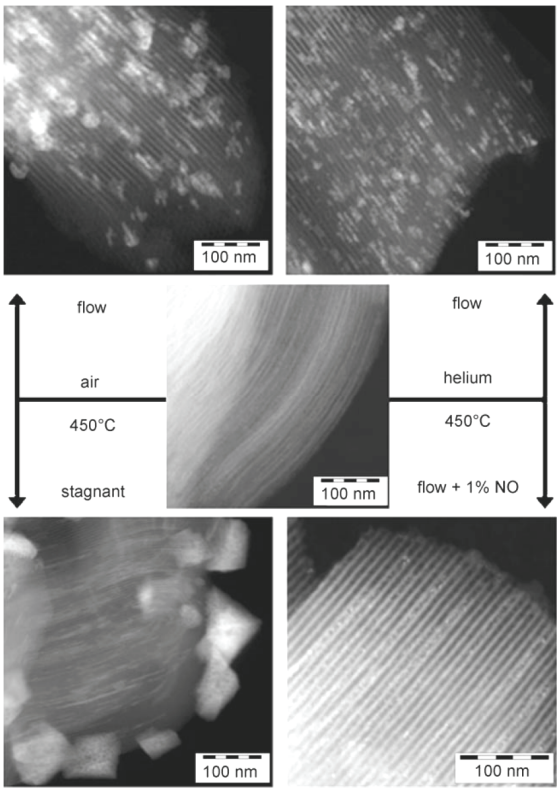

Figure 4.8. HAADF images of NiO particles formed under different synthesis conditions showing that the best dispersion and smallest size of particles are obtained after calcinations in the flow using a mixture of He and NO (Friedrich et al. 2007).

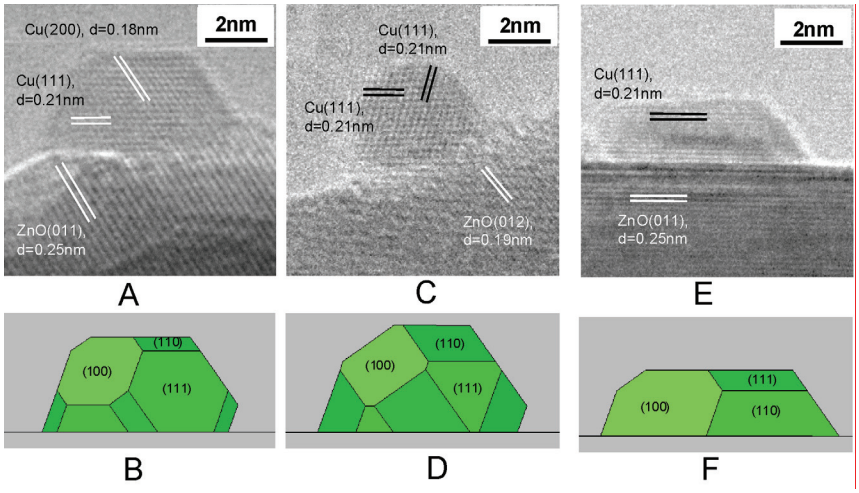

Figure 4.9. *In situ* TEM images (A, C, and E) of a Cu/ZnO catalyst in various gas environments, together with the corresponding Wulff construction of the Cu nanocrystals (B, D, and F). The images shown in A, C, and E were recorded at 220°C in a pressure of, respectively, 1.5 mbar of H_2; in a gas mixture of H_2 and H_2O, (H_2:H_20=3:1; total pressure of 1.5 mbar); and in a gas mixture of 95% H_2 and 5% CO, at a total pressure of 5 mbar. The electron beam was parallel to the [011] zone axis of Cu (Hansen et al. 2002).

Redox Process

Ceria-based oxides are commonly used as supports for three-way catalysts used in automobile catalytic converters or as anode materials in solid-oxide fuel cells. In both applications, the ease with which CeO_2 gives up lattice oxygen (reduction) in an oxygen-lean environment and takes it back in an oxygen-rich environment (oxidation)—also known as oxygen storage capacity (OSC)—determines its activity. Recently, *in situ* observations have been made using ETEM to understand atomic-level structural and chemical changes during redox reactions responsible for CeO_2's high OSC (Wang et al. 2008). A combination of high-resolution images, electron diffraction, and electron energy-loss spectra recorded between 400–800°C in 0.5-1.5 Torr of dry hydrogen gas has provided an unprecedented insight into the process.

For example, both an electron diffraction image and a high-resolution electron microscopy (HREM) image revealed the formation of a superstructure (Figure 4.10, center) during reduction. Electron energy-loss spectra recorded from the same catalyst particle confirmed Ce to be in +3 oxidation state as the Ce $M_{4,5}$ (white-line) intensity ratio reversed compared to the one recorded at 270°C (Figure 4.10, lower right and center). Moreover, the surface of the catalyst particle changed from rugged (Figure 4.10, upper right) to smooth (Figure 4.10, upper center) during reduction and did not reverse back upon reoxidation (Figure 4.10, upper left). The rugged facets expose the {111} polar surface, which is the most stable surface, and become unstable upon reduction. On the other hand, the neutral {110} surface is smooth and easy to reduce. Therefore, the ceria surface reconstructs to form stable {110} surfaces upon reduction that can be easily subjected to redox cycles.

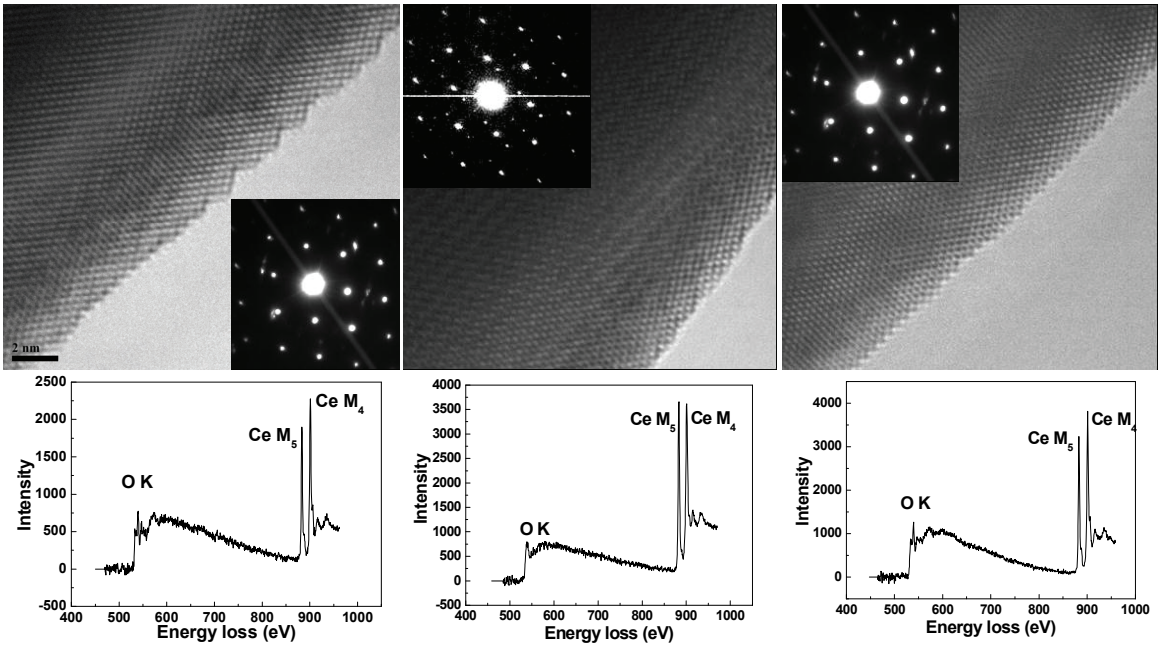

Figure 4.10. HREM images (top), electron diffraction patterns (inset), and electron energy-loss spectra (bottom) of CeO_2 particles oriented along a 110 zone axis recorded at 270°C (left), 730°C (center), and 600°C (right) in 0.5 mbar of dry hydrogen. Note the appearance of the superstructure in the center image and the electron diffraction due to oxygen vacancy ordering upon reduction at high temperature that disappeared (right image) upon cooling as ceria oxidized back. Change in the ratio of Ce $M_{4,5}$ edges was used to determine the oxidation state of Ce (Wang et al. 2008).

Catalyst Poisoning: Synthesis of Carbon Nanotubes

Transition metal catalysts are very suitable for a number of reaction processes in the petrochemical industry, such as hydrogenation, hydrocarbon hydrocracking, and Fischer-Tropsch synthesis. However, carbon

generated during these processes deposits on the catalyst surfaces, making them inactive. Under selective conditions the carbon deposit can nucleate and grow to form carbon nanotubes (CNTs) that have a number of applications in bioscience and nanotechnology. Understanding the mechanism of coke deposition on transition metal particles can help researchers find ways to control the process. It has been proposed that carbon first dissolves in the metal and diffuses out after the lattice is supersaturated to form CNTs. However, the group at Haldor Topsøe has made direct observations of the growth of carbon nanofibers using ETEM. Time-resolved images recorded during decomposition of CH_4 at 536°C show that carbon deposited on the surface steps of Ni catalyst particles nucleates and grows to form graphitic carbon nanofibers (Helveg et al. 2004). Theoretical calculations performed by Prof. Nørskov's group at the Technical University of Denmark (see site report, Appendix D) have confirmed that the diffusion of carbon on Ni surfaces is energetically favorable compared to dissolution of carbon in the Ni lattice (Abild-Pedersen et al. 2006). The Nørskov group also shows that surface steps play an important role for nucleation and growth. The WTEC panel found that this is an active area of research within the catalysis community in China but is not as active a focus area in Europe.

Similar dynamic observations are currently being applied for understanding the effects of temperature and gaseous environments on both nanostructured particles and supports. Combined with spectroscopy data, such observations can assist in understanding how to better control catalytic processes.

FUTURE TRENDS

The WTEC panel found that characterization of nanostructured catalysts under working conditions is a priority for many groups in Asia, Europe, and the United States, and different groups are approaching it in different ways. Research groups in the UK (Cambridge and Cardiff) are most active in designing experiments using scanning probe microscopes (e.g., STM and AFM) to obtain atomic-level information about surface structures at a wide range of temperatures (liquid nitrogen -1000 K) in both gaseous and liquid environments. However, researchers must be careful about the effect of tip bias on the reaction process. Also, obtaining chemical information and changes below the surface layers is very difficult.

Electron microscopes (SEM, TEM, and STEM) operate best under high-vacuum conditions and are used to obtain structural and chemical information from the nanometer to the atomic scale. While following the effects of temperature on structure and chemistry of individual catalyst particles is quite simple, determining effects in gaseous environments requires extensive modification to the sample holder or to the microscope column and still these modifications can only achieve a fraction of the gas pressures used in a reactor. Moreover, researchers must be very careful about the effect of high-energy electrons on the sample and on the reaction process. Although most of the host institutes in China mentioned *in situ* observation under reactive conditions to be important, they did not yet have the facilities. Hitachi in Japan has developed holders and a modified microscope to observe a three-way-catalyst under a reactive environment. Both Haldor Topsøe and the Technical University of Denmark currently lead the world in applying *in situ* electron microscopy measurements to catalysis. In the United States, the effort is mostly at Arizona State University, but other institutions (e.g., Purdue University) and DOE National Labs (Brookhaven and Oak Ridge) are setting up facilities for *in situ* TEM observations under reactive environments.

It is clear from the above discussion that no single microscopy technique is perfect. This realization has led to the development of systems that combine a number of techniques to observe the samples under the same reaction conditions. This is often achieved by integrating sample transfer chambers between two complementary techniques that require different operating conditions. For example, after imaging the effects of a reactive environment using STM, samples can be transferred to an X-ray photoelectron spectroscope (XPS) to obtain spectroscopy information; this is being done at ETH in Zurich, Switzerland, and the Technical University of Munich in Germany (see site reports, Appendix D). Researchers at the Fritz Haber Institute in Berlin (site report, Appendix D), are currently developing an ultrahigh-resolution spectromicroscope (known as SMART), a high-field W-band electron paramagnetic resonance spectrometer to investigate surfaces in ultrahigh vacuum, and a new low-temperature STM. The SMART utilizes both chromatic and spherical aberration corrections to overcome the resolution limitations of currently available photoelectron emission microscopes to achieve 2 nm spatial resolution and 100 meV energy resolution. They

also plan to use this instrument for near-edge X-ray absorption fine-structure, XPS, and Auger spectroscopy, as well as for diffraction methods such as microspot-LEED and photoelectron diffraction.

At Cardiff University, a hot filament deposition chamber is connected to an STM, EPR (electron paramagnetic resonance), LEED, and a preparation chamber. The same sample can be transferred from one system to the other without being exposed to air, in order to obtain imaging and various spectroscopic information from the same regions of interest.

SUMMARY

Electron and tunneling microscopy are used for routine characterization of nanostructured catalysts to correlate synthesis to properties and functions. These techniques are quite effective in obtaining nanoscale structural and chemical information during various levels of synthesis and operation. Although there is a widespread consensus on the need to observe catalysts under reactive environments, very few groups have made investments to purchase or develop the required instrumentation. Environmental SEM (ESEM) and STM are more readily available than environmental TEM (ETEM), most probably because of TEM/ETEM's high cost and operational difficulty. Also there is clearly a need to improve both temporal and spatial resolution to be able to observe atomic-level changes in the reaction time frame.

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CHAPTER 5

THEORY AND SIMULATION IN CATALYSIS

Matthew Neurock

INTRODUCTION

The past two decades have witnessed tremendous advances in the development and application of theory and simulation to catalysis. Computational catalysis has reached the stage where it has become an invaluable complement to experimental efforts aimed at understanding and controlling the reactivity of catalytic materials. The increase in computer processor speeds, the development of parallel architectures, and advances in theoretical methods have enabled the simulation of much more complex heterogeneous catalytic materials and processes. As a result, theory and simulation have lead to unprecedented advances in elucidating catalytic reaction mechanisms, establishing the influence of realistic reaction environments, and aiding in the design of new materials.

Despite this progress, the complexity of many catalytic materials along with the complexity of the reaction environments in which they operate present significant challenges for theory and simulation. Figure 5.1 presents just a few examples of current catalytic systems in order to highlight some of the differences in the types of materials and the challenges they present for theory and simulation. This includes homogeneous and supported homogeneous catalysts with complex ligand spheres; metal particles of different sizes, morphologies and compositions anchored to different supports; well-defined nano-oxide clusters and porous materials such as polyoxometallates and zeolites; and ill-defined metal oxides, sulfides, carbides, and nitrides, just to name a few. In addition to the material structures, the reaction media and the local environments in which the catalytic transformations are carried out is becoming increasingly more complex, involving the presence of solution, mixed solvents, ionic liquids, and complex melts.

The ability to design such complex materials will undoubtedly require a fundamental understanding of the active site, the elementary transformations that occur at the site, and the influence of the reaction environment under working conditions. Advances in the design of such systems and their industrial applications will therefore require traversing a very diverse spectrum of time and length scales, ranging from the electronic structure that controls the chemistry at the active site, to the detailed atomic structure of supported particles, on up to the performance of the entire catalytic process. The methods that are currently used to model particular features such as the atomic structure of a material or temperature and composition profiles in a reactor, currently exist as shown in Figure 5.2. However, the ability to traverse across different time and length scales, which is important in accessing how the changes in the atomic structure of the catalyst ultimately influence catalytic process performance, presents a number of difficult challenges. While the seamless integration across the full spectrum of time and length scales presents a tremendous challenge that will not be solved anytime in the near future, we are beginning to see the combining of methods to cross time-and length-scale boundaries, as will be discussed in this chapter.

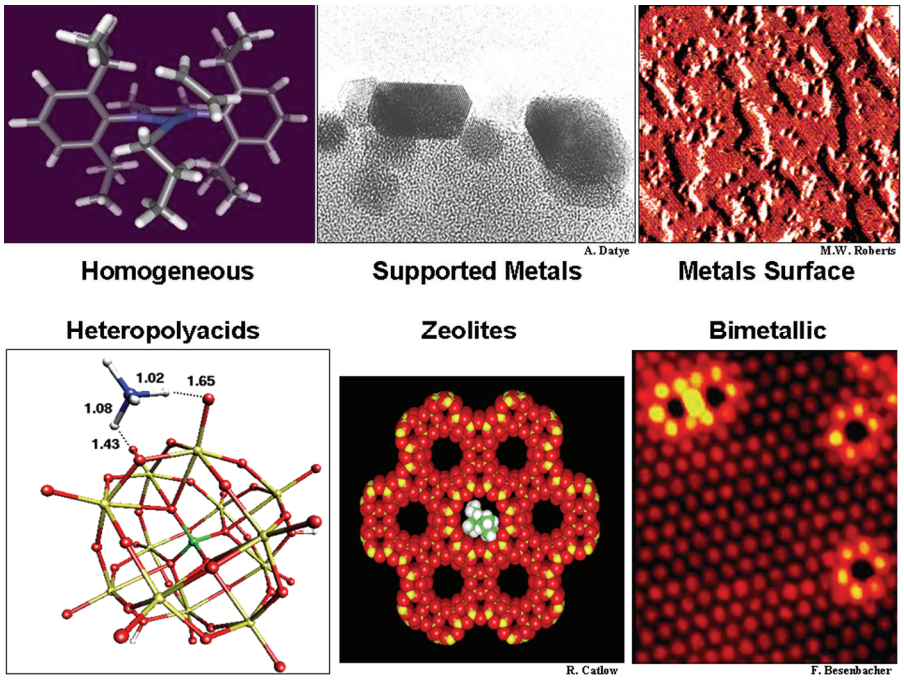

Figure 5.1. Structure and complexity of different catalytic materials.

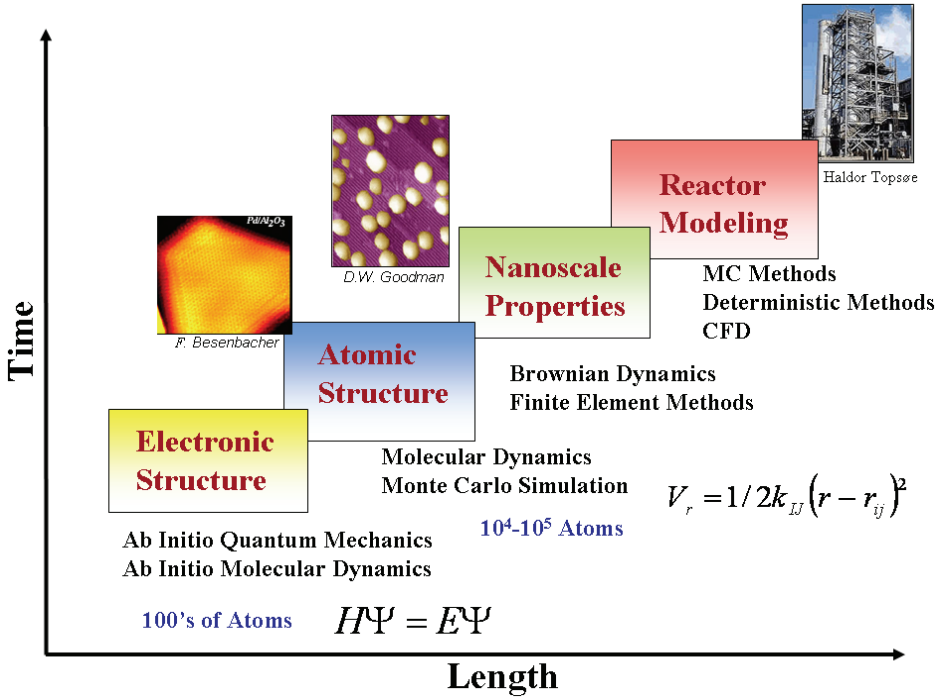

Figure 5.2. Hierarchy of time and length scales in heterogeneous catalysis, and associated modeling methods.

COMPUTATIONAL CATALYSIS: WHERE ARE WE TODAY?

The results from the WTEC panel's assessment clearly reveal that theory and simulation have made important advances and are now able to:

- Predict structure and properties of model catalytic systems.
- Complement and resolve spectroscopic measurements by simulating the resulting spectra.
- Elucidate catalytic reaction pathways and mechanisms
- Begin to guide the search for new catalytic materials.

METHODS AND THEIR APPLICATION

Computational catalysis is typically defined by the methods that link the detailed electronic structure to catalytic performance (the first 2–3 boxes in Figure 5.2). This involves the determination of structure and chemical properties, intrinsic catalytic reactivity, and the simulation of catalytic kinetics, which are best modeled by quantum mechanical methods, atomic scale simulations, and kinetic simulations. A very short review of each of these areas and their application is presented below. More detailed discussions on these methods are presented elsewhere (e.g., van Santen and Neurock 2006).

Electronic Structure Methods

The ability to simulate reactivity ultimately requires the solution of Schrödinger's equation as it involves making and breaking chemical bonds and thus the ability to follow changes in the electronic structure. Reactivity can only be resolved then by methods that follow the changes in the forces on the electrons and the nuclei. There are a wide range of electronic structure methods that can be classified as (1) semi-empirical, (2) *ab initio* wave function, and (3) density functional theory (DFT) methods (Head-Gordon 1996; Leach 1996; Jensen 1999). All of these methods start with the time-independent solution to the Schrödinger's equation and make a series of assumptions in order to solve the force balance that results on the N-particle (proton and electron) system. Ultimately, our inability to directly solve the multicenter integrals that result from the electron-electron interactions lead to the three different approaches presented. Semi-empirical methods avoid the solution of the multicenter integrals by fitting the results to experimental data. The success for transition-metal-based systems, however, has been very limited. While early studies in catalysis used these methods to provide qualitative understanding, they have for the most part been replaced by *ab initio* wave function or density functional theory studies.

Ab initio wave function methods involve the solution of the structure and the energy of the N-electron wave function by making a sequence of approximations that allow one to decouple the N-electron system into one that involves the solution of N single electron systems. These assumptions lead to the simplest solution strategy, which is known as the Hartree-Fock (HF) solution. The HF solution avoids the direct electron-electron interactions, solving them instead via a mean-field approach (Head-Gordon 1996; Leach 1996; Jensen 1999). This is a gross oversimplification that misses out on the correlated electron motion that results from the direct interactions between electrons. These interactions can be accounted for but require much more rigorous calculations.

The accuracy of *ab initio* wave function methods can be systematically improved by moving to more complete descriptions of the configurational interactions (CI) and basis functions used to describe the wave function. An infinite accounting of the configurational interactions and an infinite basis set expansion would lead to the exact energy of the N-particle problem. As the CI and basis function limits are extended, the size of the system that can be solved becomes significantly smaller (Head-Gordon 1996; Jensen 1999). While CI calculations can be carried out on cluster models for catalytic systems, they are limited to clusters that are less than 50 heavy atoms. While these methods have been useful for homogeneous catalytic systems, there have been very limited applications to more complex heterogeneous systems, as they are limited by system size.

Quantum Monte Carlo (QMC) methods offer a second approach to accurately model electron exchange and configuration interactions. While QMC methods are formally less costly than *ab initio* CI methods, they have their own set of drawbacks in terms of finite size effects that require large unit cells, the lack of analytic second derivatives and force predictions, and significant challenges in modeling transition metals (Carter 2008).

The development of density functional theory has had a tremendous impact on computational heterogeneous catalysis as it has allowed for the solution of systems that offer more realistic models of the active site and the catalyst surface. In the original formulation, Hohenberg and Kohn (Hohenberg and Kohn 1964; Kohn and Sham 1965) showed that the ground state energy for a system is uniquely described by a functional of its electron density. Kohn and Sham later extended this to practice by showing how the energy could be divided into kinetic energy, attractive nuclear-electron interactions, and an exchange-correlation term, all of which could be described as a functional of the density. While this is an exact approach to solve for the energy of the system as a functional of the density, there is no formal way in which to determine the exchange correlation functional.

Current acceptable solutions involve calculating gradient-corrections to the local approximation for the correlation and exchange energies (Becke 1986; Perdew et al. 1992). Despite these corrections, the accuracy of DFT is still limited, and thus this is a very active area of research in theoretical chemistry. Since the electron density is the fundamental entity, DFT tends to scale as N^3 where N is the number of electrons. In comparison, *ab initio* many-body perturbation methods and higher-level CI calculations tend to scale from N^5–N^7. Density functional theory thus allows for the simulation of systems that contain up to a few hundred atoms. This proves to be useful in determining the adsorption energies and reactivity on well-defined single-crystal surfaces as well as within zeolites. In terms of absolute accuracy, density functional theory is typically within 20 kJ/mol (van Santen and Neurock 2006). There are, however, known outliers. In addition, DFT fails to appropriately account for weak dispersion forces. For systematic trends, DFT is even more accurate and in many cases can be system-dependent. Coupled-cluster theory can be used to provide accuracy to within a 2 kJ/mol but is typically limited to systems of the size of 10 atoms (Head-Gordon 1996; Leach 1996; Jensen 1999; van Santen and Neurock 2006). While method accuracy is certainly important, it must also be balanced with model accuracy that refers to the size of the system used to model the active site. DFT has thus provided an important impact in the field, because it tends to balance both method and model accuracies.

The advances in both wave function methods and density functional theory now allow us to simulate both the electronic and the geometric structure for a specific system with a reliable degree of accuracy. They can also be used to elucidate transition states and thus determine activation barriers as well as rate constants by invoking transition state theory or variational transition state theory. The advances in density functional theory as well as the advances in computation have now made it possible to simulate complex networks of elementary steps over model substrates in order to determine actual catalytic performance, such as activity and selectivity, and in addition, these advances provide the ability to resolve reaction mechanisms.

Ab initio methods in principle can be used to simulate a wide range of structural, electronic, or energetic properties of the system. This has led to tremendous advances in simulating the spectroscopic interrogation of the state of the surface or the adsorbed intermediates on the surface. For example, the calculation of second derivatives of energy with respect to changes in the atomic positions can be used to calculate the vibrational frequencies of an adsorbed intermediate, which can then be directly compared with those from infrared or Raman spectroscopy. DFT is typically within about 5% of the actual spectra (van Santen and Neurock 2006). Similarly, theory can be used to simulate nuclear magnetic resonance shifts and optical spectra such as ultraviolet visible (UV) shifts and nuclear magnetic shifts. The accuracy for DFT predictions of these properties is typically less. Band gaps, for example, are only good to within about 0.5 eV. Higher-level methods and new functionals, however, have resulted in significantly more accurate descriptions for particular systems (Staroverov et al. 2004; Hafner 2008).

Embedding methods have been developed in order to expand the model size without sacrificing the accuracy of the electronic structure and reactivity at the active site that carries out the chemistry. Embedding involves linking an active site region, which is described by a higher level *ab initio* method such as density functional

theory, to an outer shell, which is described by a lower-level method such as HF or molecular mechanics (Sauer 1994; Whitten and Yang 1996; Govind et al. 1999; Froese and Morokuma 1999; Vreven and Morokuma 2000). This is typically done by defining a region of overlap where the two descriptions meet. While these methods provide the ability to simulate much larger systems, there are still issues with appropriately establishing how the inner reactive zone is linked to the outer region. This approach has been quite useful in simulating zeolites where the outer Si-O framework can appropriately be handled by lower-level calculations (Sauer 1994).

Atomic and Molecular Simulations

While the simulation of reactivity requires an accurate accounting of the electronic structure, there are many important questions that are focused on structure or thermodynamics rather than on reactivity. As such, the electron density is not very important and the fundamental entity then becomes the atom. Atomic-scale simulations track the interatomic interactions that govern both structure and dynamics and ignore the electronic structure. The interactions are modeled by force fields, which are determined *a priori* from experimental regression or through *ab initio* calculations. The force fields are based on atomic (intra- and inter-molecular) interactions to the potential energy that result from changes in the bond length, bond angle, torsion angle from their standard positions, as well as Coulombic and van der Waals intermolecular forces (Leach 1996; Cummings 2002).

Energy minimization algorithms are perhaps the most basic simulation methods employed in catalysis. They are typically used to optimize complex material structures. Simulated annealing strategies are often employed to help isolate the lowest energy states. Energy minimization schemes are routinely used to help determine the structure of metal and metal oxide surfaces and particles as well as complex and porous oxides. While these simulations are easy to carry out and offer very useful information, they require reliable interatomic potentials for the materials of interest.

The thermodynamic properties for an N-particle (atoms or molecules) system can be determined from statistical mechanics. Monte Carlo simulation methods are typically used in order to integrate the configurational integral and solve for various thermodynamic properties. Various methods have been used in the literature to simulate different properties. The properties of interest typically dictate which methods are used (Leach 1996; Bell, Maginn, and Theodorou 1997; Cummings 2002).

The three most widely adopted methods in catalysis are the Canonical, Grand Canonical and Gibbs Ensemble Monte Carlo simulations which are used to determine the pressure, sorption properties, and phase behavior for different catalytic systems (Leach 1996; Bell, Maginn, and Theodorou 1997; Cummings 2002). Canonical simulations hold the number of molecules, volume, temperature, and unit cell constant and are typically used to minimize the Helmholtz energy of a system and establish the resulting pressure. Grand Canonical Ensemble Monte Carlo (GCMC) simulations hold the chemical potential, the volume, and the temperature constant in order to determine the optimal number of particles. GCMC simulations are typically used to simulate equilibrium sorption in microporous systems such as zeolites (Bell, Maginn, and Theodorou 1997). Gibbs Ensemble Monte Carlo simulations act to minimize the Gibbs free energy and have also been used to simulate sorption behavior as well as phase equilibria.

Dynamics

The simulation of dynamics requires models that can follow temporal changes in structure. Classical systems are solved by simply integrating Newton's equation of motion to determine the time-dependent behavior of the atoms or molecules (Allen and Tildesley 1987; Frenkel and Smit 1996; Leach 1996). These simulations are based on forces that act upon the atoms at any given time and thus require accurate force fields. The integration of the forces that act upon each atom within the system provides the time-dependent changes in position and the velocities in the systems. Molecular dynamics (MD) simulations have been used to simulate a range of dynamic properties for catalysis, including diffusion, transport, temporal changes in the catalyst surface structure, and the structural changes in an external fluid media with time (Bell, Maginn, and Theodorou 1997).

Reaction systems require the ability to follow the dynamics of the atomic nuclei as well as the electrons. There are currently three different approaches to simulate the dynamics of reaction systems: (1) quantum dynamics, (2) *ab initio* molecular dynamics, and (3) Car-Parrinello molecular dynamics (van Santen and Neurock 2006). Quantum dynamics fully treats both the dynamics of the electrons as well as the nuclei. These are very expensive simulations and have been used predominantly to follow the dynamics of in the collisions of very small molecules such as hydrogen, nitrogen, and methane on ideal surfaces.

Ab initio molecular dynamics methods are far less expensive, because they invoke the Born-Oppenheimer approximation in order to decouple the movement of the electrons and the nuclei. *Ab initio* methods are then used to calculate the forces on each of the atoms at a particular instant in time. The forces are used to solve Newton's equation of motion for very small time steps which provides the new positions of the nuclei. *Ab initio* methods are subsequently used to calculate the energies as well as the forces at this new position and time. This constant alternation between *ab initio* calculations and classic dynamics simulations is continued in order to map out the time dependent properties of the reaction system.

The final approach, developed by Car and Parrinello (1985), treats the electrons as "particle-like" and assigns fictitious masses to them. This allows the electrons to be propagated together in time with the nuclei, which significantly speeds up the calculations since quantum mechanical (QM) calculations are not required after every step. The latter two approaches have been used to simulate both homogeneous as well as heterogeneous catalytic systems that occur in the solution phase.

Kinetics

The ability to move from detailed electronic structure to catalytic kinetics requires some form of coarse graining in order to traverse the disparate time and length scales. The classic approach to simulating kinetics involves the solutions to a set of differential equations that describe the formation and destruction of all of the reaction intermediates that result from the controlling reaction paths. Dumesic (Dumesic et al. 1993) pioneered the microkinetic approach, which involves modeling the elementary paths that comprise the mechanism. The activation energies from detailed *ab initio* calculations can be used together with transition state theory to provide the input required to solve the resulting differential equations and follow the kinetic behavior of the system.

A second approach to modeling kinetics takes advantage of stochastic kinetic approaches that maintain the detailed structure and positions of atoms in the surface and the adsorbed molecules. This avoids the loss of atomic structural information concerning the surface that is inherent in deterministic models due to the early averaging that is required (van Santen and Neurock 2006). As such, one can explicitly track the atomic surface structure and individual molecular transformations. The same set of elementary surface processes can now be simulated together with the atomic surface structure. Monte Carlo techniques are typically used to solve these stochastic systems. A wide range of different catalytic kinetic systems have been modeling using kinetic Monte Carlo simulations methods, including temperature programmed desorption, temperature programmed reaction, transient kinetics, and steady state kinetics (van Santen and Neurock 2006).

SNAPSHOT OF THE EFFORTS IN EUROPE AND ASIA

While there are outstanding efforts in the development and application of theory and simulation to catalysis going on throughout the world, the WTEC study focused on Europe and Asia. A summary of the sites that the WTEC panelists visited as well as other sites with strong programs in computational catalysis is given in Tables 5.1 and 5.2. The tables do not capture all of the scientists working in computational catalysis but instead provide a snapshot of what is happening in both regions. A detailed analysis of the findings indicates that there are characteristic differences among Europe, Asia, and the United States.

Table 5.1. Important European Sites & Activities in Computational Catalysis, Theory, and Simulation

AUSTRIA

Juergen Hafner, Georg Kress, *University of Vienna*
Structure, electronic chemical properties of metals, metal oxides, metal sulfides and zeolites; *ab initio* method development (VASP)

DENMARK

Jens Nørskov, Thomas Bligaard, Jens Rossmeisi, *Technical University of Denmark
Catalytic reactivity of metals, metal alloys, metal oxides, metal sulfides, and zeolites for steam reforming; oxidation; direct NO decomposition; PEM and solide oxide fuel cells; ammonia synthesis & decomposition; *ab initio* method development (DECAPO)

Bjork Hammer, *University of Aarhus*
Surface chemistry and catalytic reactivity of metals and metal alloys

FRANCE

Philippe Sautet, Francoise Delbecq, David Loffreda, Univ. of Lyon; *Ecole Normale Supérieure of Lyon*
Surface catalyis on metals, alloys, supported organo-metallics, aluminum oxide surfaces, integration of theory and spectroscopy

Pascal Raybaud and Hervé Toulhoat, *IFP
Molecular modeling, *ab initio* thermochemistry of catalytic surface, catalytic reactivity, transition metal sulfides for hydrodesulfurization, aluminum and titanium oxides for catalytic supports, active phase-support interaction, hydrogenation

Nicolas Bats, *IFP*
Guided synthesis and discovery of microporous materials

(*) **Christian Minot, *Université Pierre et Marie Curie***
Ab initio applications to metal oxides and metal oxide catalyzed reactions

Odile Eisenstein, Jean-Sébastien Filhol, Marie-Liesse Doublet, Frédéric Lemoigno, *Univ. of Montpellier*
Supported organometallics, electrocatalytic and photochemical systems

Jean-François Paul, *University of Science and Technology of Lille*
Hydrodesulfurization catalysis

GERMANY

Joachim Sauer, *Humboldt University*
Oxidation and acid catalysis over metal oxides, zeolites, method development

Matthias Scheffler** (& Karsten Reuter)**, *Fritz Haber Inst.
Oxidation catalysis over metal oxides, surface kinetics, *ab initio* and statistical mechanical developments

Notker Roesch, *Technical University of Munich
Catalysis over metal particles, steam reforming, metal particle/oxide support interfaces, DFT developments

Klaus Hermann*, *Fritz Haber Institute
Surface crystallography, structure/reactivity/spectroscopy of metal oxides, theory development (StoBe)

Frerich Keil, *Technical University of Hamburg*
N_2O, and adsorption & diffusion simulations, in zeolites

Axel Gross*, University of Ulm*
Chemisorption and reactivity on metals

ICELAND

Hannes Jonsson, *University of Iceland*
Surface reactivity of metals; *ab initio* methods development

ITALY

Gianfranco Pacchioni, *University of Milan*
Structure and reactivity of metal oxides, metals and supported metals, role of defects

Roberto Dovesi, Roberto Orlando, Carla Roetti, Cesare Pisani, V. Saunders, Piero Ugliengo, *University of Turin
Structure and reactivity of metal oxides and zeolites, *ab initio* method development (crystal)

SPAIN

Francesc Illas, *University of Barcelona*
Catalysis over transition metal and alloy surfaces; metal-metal oxide interfaces, electrochemical effects

Avelino Corma, *University of Valencia
Combined theory and experiment for zeolites and transition metals

Javier Santz, *University of Seville*
Metal and metal oxide surfaces and interfaces

SWITZERLAND

Alfons Baiker, *ETH
Theory and spectroscopy to understand the chiral modifiers to metal surfaces.

THE NETHERLANDS

Rutger van Santen (and Tonek Jansen), *Eindhoven University of Technology
Zeolite catalysis, catalysis over metals for a wide range of reactions, *ab initio* applications, and development of molecular simulations, theory, and experiment

Mark Koper, *Leiden University*
Electrocatalysis theory and experiment

Berend Smit, *University of Amsterdam* (now at Berkeley)
Adsorption, diffusion, and reactions in porous materials

Geert-Jan Kroes, *Leiden University*
Quantum dynamics of dissociative adsorption on metals

UNITED KINGDOM

Richard Catlow, *University College London*
Structure and reactivity of complex micro/mesoporous catalytic materials, zeolites; molecular simulation method development

Peijun Hu, *Queens University, Belfast*
Structure and reactivity of metal surfaces for water gas shift, Au catalysis, Fischer-Tropsch synthesis

David King, Steven Jenkins, *University of Cambridge
Reactivity of metal surfaces; combination of theory and experiment

David Willock, *Cardiff University
Metals and zeolites

* Sites visited by WTEC panelists during the study
(*) Dr. Minot was not present; panelists did not see his lab.

Europe

Computational catalysis has a long history in Europe. There is a core group of well-established scientists who have been instrumental in the success of theoretical methods and their application to catalysis over metals, metal oxides, metal sulfides, and zeolites. Most of the solid state electronic structure codes that are currently used throughout the world to model heterogeneous catalytic systems were developed in Europe by leading theoretical physics and chemistry groups. Those include the following:

- *CASTEP (Cambridge Serial Total Energy Package)*: Michael Payne and colleagues, Cambridge University (Segall et al. 2002)
  http://www.castep.org
  Commercial code offered by Accelrys, Inc.
- *VASP (Vienna Ab Initio Simulation Package)*: Juergen Hafner, Georg Kresse, and colleagues, University of Vienna (Kresse and Hafner 1993; Kresse and Furthmüller 1996a and 1996b)
  http://cms.mpi.univie.ac.at/vasp
- *DACAPO*: Jens Nørskov and colleagues, Danish Technical University
  https://wiki.fysik.dtu.dk/dacapo
- *CRYSTAL*: C. Pisani, R. Dovesi, C. Roetti, and colleagues, University of Turin (Pisani and Dovesi 1980; Saunders 1984; Pisani, Dovesi, and Roetti 1988)
  http://www.crystal.unito.it/
- *ADF BAND (Amsterdam Density Functional Theory)*: Professor Evert Jan Baerends and colleagues, Free University of Amsterdam (Philipsen et al. 1997; Velde et al. 2001)
  http://www.scm.com/
  Commercial code offered by SCM, Inc.
- *DMOL3*: Professor Bernard Delley and colleagues, Paul Scherrer Institute (Delley 2000a and 2000b)
  http://accelrys.com/products/materials-studio/modules/dmol3.html
  Commercial code offered by Accelrys, Inc.

In addition to the development in Europe of solid state methods, there have also been important developments in embedding methods and atomistic simulations that allow for the simulation of much larger and more realistic environments for both zeolites and metal oxides.

- *QMPOT*: Joachem Sauer and colleagues, Humboldt University
  (Eichler, Kolmel, and Sauer. 1997; Sauer and Sierka 2000)
- *GULP*: Richard Catlow and Julian Gale, University College London
  (Gale 1997; Gale and Rohl 2003)
  Commercial code offered by Accelrys, Inc.

These codes are used throughout the world, and many have been adopted into commercial codes as well.

Europe has also led much of the efforts in the theory of heterogeneous catalysis, with strong efforts by well-established scientists who have been active in the field for over 30 years. Much of the current theory that governs metal, metal oxide, metal sulfide, and zeolite catalysis has been the result of leading efforts in Europe. A list of some of the established groups in each area is given below. An important point worth noting is that essentially all of the efforts in Europe reside in the basic sciences, i.e., Chemistry and Physics.

- *Metals*: Jens Nørskov (Denmark), Matthias Scheffler (Germany), Notker Rösch (Germany), Francesca Illas (Spain), Philippe Sautet (France)
- *Oxides*: Gianfranco Pacchioni (Italy), Matthias Scheffler (Germany), Klaus Herrmann (Germany), Joachim Sauer (Germany), Christian Minot (France), Pascal Raybaud and Hervé Toulhoat (France), Malgorzata Witco and Jerzy Haber (Poland), Lars Peterson (Sweden)
- *Sulfides*: Jens Nørskov (Denmark), Pascal Raybaud and Herve Toulhoat (France)

In addition to these established programs, there is an increasing number of younger faculty members in Europe who have strong efforts in ancillary electronic structure developments and their application to more complex materials and their environments. Their activities are also listed in Table 5.1.

Asia

There was very little discussion of theory and simulation at the sites that the WTEC panelists visited in Japan, China, and Korea. The panel findings, as well as a few of the well-established sites known for strong efforts in computational catalysis in Japan, are highlighted in Table 5.2.

Table 5.2. Important Asian Sites & Activities in Computational Catalysis, Theory, and Simulation

CHINA	JAPAN
Guichang Wang, ***Nankai University*** Reactions over metal surfaces	**Akira Miyamoto,** ***Tohoku University*** Development of novel *ab initio*-based molecular dynamics methods, simulation of NO_x reduction, photocatalysis, oxidation, zeolites, combinatorial catalysis
W.K. Chen, ***Fuzhou University*** Methanol and N_2O decomposition on metal and metal oxide	**Hisayoshi Kobayashi,** ***Kyoto Institute of Technology*** Photocatalysis, splitting of water, doping metal oxides, oxidation over metals
Zhi-Pan Liu, ***Fudan University*** CO oxidation on metals, Fischer Tropsch synthesis	*__AIST__ Photocatalysis
Zhaoxu Chen, ***Nanjing University*** Water dissociation on metals	**KOREA**
Daiqian Xie, *Nanjing University* Methane dissociation on metals	*__Jae Sung Lee,__ ***Pohang University*** DFT calculations of band gaps, band edges, and optical absorbance for photocatalysis
*__Haijun Jiao,__ ***Chinese Academy of Science, Taiyuan*** Fischer Tropsch synthesis	
Q. Jiang, ***Jilin University*** Ethylene epoxidation on Ag(111)	
	* Sites visited by WTEC panelists during the study

The theoretical and simulation efforts for catalysis in Japan are strong but tend to be concentrated in just few laboratories. This is a characteristic of Japanese research programs in general, in which there are just a few groups but very strong concentrated programs. In particular, Professor Akira Miyamoto and Professor Hisayoshi Kobayashi are internationally known for their important contributions to computational catalysis.

Professor Miyamoto has led the development of *ab initio* molecular dynamics codes, novel *ab initio* tight-binding molecular dynamics methods, and combinatorial informatics algorithms. The work of his group covers a broad range of different catalytic materials, including rare earth oxides, titanosilicates, metal oxides and metals, as well as a range of different applications, including NO_x reduction, decomposition of volatile chemicals, methanol synthesis, Fischer Tropsch synthesis, photocatalysis, and Ziegler-Natta polymerization catalysis. The Miyamoto group is comprised of over 80 researchers; these include 9 visiting professors, 3 visiting assistant professors, 6 associate professors, 2 assistant professors, 3 research fellows, 3 cooperative researchers, and 53 students or technical staff. This is perhaps the largest effort in theory in the world, but not all of the researchers are focused on catalysis.

The work in the Professor Kobayashi group has a strong focused effort on modeling photocatalysis and electrocatalysis. The work is closely coupled with strong experimental efforts at different institutions in Japan. There are also strong efforts at AIST, which are focused on modeling photocatalytic systems.

Historically, the efforts in theory and simulation for catalysis in China have been much less significant than those in Europe and the United States. This may have been the result of either the significant expense for high-performance computing or the lack of specific training in this area. The availability and affordability of high-speed computing and electronic structure methods, however, have recently fueled a significant increase in the number of researchers and published papers in this area. In addition to the increased computational availability, there are a number of the younger scientists who have worked with some of the leading theory and catalysis groups in Europe and in the United States as postdoctoral fellows and have since returned to China as assistant professors. The efforts in theory and simulation in China have almost all been focused on the application of electronic structure methods to model metals, metal oxides, metal sulfides, and mesoporous

catalytic materials, and the reactions they catalyze. Most of these efforts are focused on energy conversion processes. The scientists in computational catalysis are nearly all assistant professors. These scientists tend to be single investigators who are spread across China and tend to be less connected with experimental efforts. This is unlike the efforts in Europe and Japan in which theory and simulation are found in larger groups and are more directly tied to experiment. The WTEC panel found few efforts in Korea with the exception of the group of Professor Jae Sung Lee at Pohang University who was using theoretical calculations to complement experimental efforts in determining the optical properties of different photocatalytic materials.

Comparison of Europe, Asia, and the United States

If one compares the nature of the research, the experience of the researchers, and the infrastructure for research, there are some clear differences among Europe, Asia, and the United States. As discussed above, the research effort in Europe is well-established and has been carried out by distinguished scientists in Chemistry and Physics who have pioneered the development and application of *ab initio* methods to catalysis over the past three decades. This includes very strong efforts in Denmark, France, Germany, Italy, the Netherlands, Spain, and the United Kingdom. There has been an almost linear increase over time in the addition of young faculty in computational catalysis across Europe in order to offset current and near-future retirements. There are a few exceptions, however, such as at the Technical University of Denmark, where a significant grant from a private foundation has helped to establish a very strong program in the computational design of catalytic materials and to hire outstanding young faculty.

The efforts in Japan are focused in just a few institutions and are run by well-established faculty. While there are strong efforts in method development, such as the development of novel QM/MD simulations and combinatorial methods, most of the work is focused on the application of theory and simulation to different catalytic systems with strong programs in photocatalysis.

In contrast, computational catalysis in China is increasing exponentially and is comprised universally of young faculty who are dispersed throughout China. The computational programs, however, do not appear to be very well connected with the experimental programs.

The efforts in theory and simulation in the United States have grown significantly over the past 15 years. While there have been a number of earlier pioneers in the field in chemistry, the efforts were perhaps more fragmented as programs stretched across a range of material systems. In addition, relatively few of the many young theoretical or computational chemists hired into chemistry or physics departments have focused on heterogeneous catalysis. Their efforts have focused instead on novel theoretical and computational method developments, drug design, enzyme chemistry, and other biological systems. This may be due to the fact that catalysis is typically viewed in the United States as a technology rather than as a basic science. As a result, there has been much more funding for biomaterials and biocatalysis than for heterogeneous catalysis. Although the number of researchers focused on heterogeneous catalysis is smaller than the number focused on biocatalysis, those in the field have been instrumental in developing novel electronic structure algorithms and modeling for both homogeneous as well as heterogeneous catalysis.

While over the past decade there have been few new faculty members in Physics and Chemistry hired in the United States to work in computational heterogeneous catalysis, there has been an exponential growth in young faculty hired into Chemical Engineering over this time period. This is perhaps a natural result of a continuing shift in Chemical Engineering to move from understanding classic macroscopic behavior to the elucidation of fundamental molecular-level science. In terms of modeling, there has been a shift from continuum-level modeling to molecular-level simulations. Molecular simulation has been a core strength in U.S. Chemical Engineering. This shift to more detailed simulations to establish the fundamental science has now begun to move into simulating electronic structure and its influence on catalytic behavior. The emphasis has been focused on the application of *ab initio* methods.

The development of electronic structure methods, however, requires a large concerted effort, with a strong basis in solid-state physics. This creates a considerable challenge for young assistant Chemical Engineering professors, who are required to show significant productivity in their first few years in order to receive

tenure. The electronic structure codes that are used today have been developed over a number of years by a strong concerted commitment. The funding and tenure situation in the United States makes the development of such electronic structure codes in Chemical Engineering departments much more difficult. The United States, however, has traditionally pioneered many of the leading efforts in atomistic and molecular-level simulations in catalysis. The strong foundations of molecular thermodynamics and kinetics that are taught in the U.S. Chemical Engineering curriculum is perhaps the major driving force for this. There has been a shift, however, over the past decade from atomistic-scale simulation development efforts to the application of *ab initio* methods. The application of both electronic structure methods and simulations has changed over the past decade as the focus of the funding agencies has changed. Most of the current efforts have targeted energy. This includes efforts in gas to liquids, electrocatalysis for fuel cells, conversion of biorenewables, and photocatalysis.

UNIVERSAL TRENDS

The Good News

The assessment from the WTEC site visits together with an analysis of the recent literature revealed some clear universal trends across the field of computational catalysis:

- Strong coupling between theory and experiment
- Simulation of more realistic reaction environments
- Isolation of factors difficult or impossible to achieve experimentally
- Applications moving to energy-related issues
- Slow improvement in method accuracy
- Invaluable partnership of theory and experiment

These trends highlight some of the important advances that theory and simulation have made over the past decade. For example, it is now possible to provide structural information such as bond lengths and angles concerning the surface structure or molecules bound the surface to within 0.05 Å and 2^{o}, respectively, and spectroscopic signatures of adsorbed intermediates to within a few percent of experiment (Forseman and Frisch 1996; van Santen and Neurock 2006). Similarly, theory can readily determine adsorption energies, reaction energies, as well as activation barriers for important elementary steps within reasonable time frames (1–2 days) and accuracies (< 20 kJ/mol), which provides a strong framework for elucidating reaction mechanisms. Theory has thus become an invaluable partner with experiment in understanding catalytic reaction systems. In addition, there appears to be growing trend around the world where theory and simulation are being used to help guide the search for new materials.

The advances in coupling theory and experiment have come from improved computational abilities as well as a greater acceptance of theory and simulation in the experimental and the industrial communities. The exponential advances in raw computational speed, increased memory, improved algorithm development, and massively parallel architectures have allowed simulations to move to much larger systems and more realistic reaction environments in reasonable time frames. Much of the theoretical work up until this past decade was focused on the chemisorption and reactivity of small molecules (< 5 atoms) on ideal single crystal surfaces carried out at very low coverages. This work provided a wealth of useful information and aided ultrahigh-vacuum surface science studies but offered few direct insights into catalysis at operating conditions. Advances that have occurred over the past few years, however, have made it possible to follow the reaction chemistry as well as a reliable portion of the local catalytic reaction environment, which includes more realistic metal clusters, metal-support interactions, higher surface coverages, the influence of alloying, solution effects, and even the presence of electric fields.

Theory in particular is being used to elucidate properties that would be difficult, and in a number of cases impossible, to determine experimentally in order to provide insights as to what controls intrinsic reactivity and catalytic chemistry. There are increasing efforts aimed at interrogating the electronic, entropic, and

intramolecular interactions that control the nature of the transition states and reactive intermediates for specific molecules.

In addition to the advances in system size and the time required to carry out particular simulations, there have also been important improvements in the methods, which have helped to improve method accuracy. For example, there are new exchange-correlation functionals that provide a more exact accounting of the exchange integrals as well as the implementation of many-body perturbation theory, namely GW theory (Hedin 1965; Hedin and Lundqvist 1969; Hybertsen and Louie 1986; Hafner 2008) to calculate self interactions and the screened Coulomb potential. This provided more accurate predictions of band gaps and excited state properties for particular materials, as well as more accurate ground state properties. In addition, higher level *ab initio* methods are being implemented that can explore much more complex surfaces as well as the nature of the reaction centers more rapidly and thus allow for significantly higher accuracies.

It was clear from the WTEC site visits as well as what is present in the current literature that theory and experiment are increasingly valuable partners and offer powerful contributions to help determine reaction intermediates, elucidate the nature of active sites, establish reaction mechanisms, and search for new materials.

The Not-So-Good News

Despite the significant advances and the exponential increase in the use of theory and simulation, there are still a number of important limitations. Some of those established in the WTEC assessment are given here:

- Method accuracy is still an issue
- Connection to actual kinetics is still weak
- Few efforts exist to link *ab initio* methods and atomistic simulations necessary to describe coupled adsorption, diffusion, and reaction
- Simulating photoexcitation and photocatalysis is a difficult challenge
- A significant shift has occurred in emphasis, from development to application

There have been a number of advances in theory, which include the development of new exchange-correlation functionals for density functional theory (Heyd and Scuseria 2003; Tao et al. 2003; Perdew et al. 2004; Staroverov et al. 2004; Perdew et al. 2005; Csonka et al. 2007; Janesko and Scuseria 2007; Tao et al. 2007; Hafner 2008; Tao et al. 2008), novel embedding schemes (Govind et al. 1999; Sauer and Sierka 2000; Vreven and Morokuma 2000), and many-body perturbation methods for surfaces (Hafner 2008). Despite these advances, the accuracy in predicting adsorption energies, reaction energies, and activation barriers is still 0.2 eV with known pathological outliers. This prevents accurate kinetic predictions, which require 0.05 eV or less. There are also no systematic ways known to improve the accuracy of density functional theory, which provides the foundation of most of the work in theory for catalysis.

While there has also been a significant increase in the application of theory to catalysis, most of the work has been focused on the calculation of single elementary steps and their energies, with little regard for the myriad simultaneous kinetic processes or the operative catalytic kinetics. Speculations on the steps that control catalysis are often made from a simple idealized potential energy surface without concern for the surface coverages, reaction rates, and competing pathways.

In many catalytic systems, adsorption, diffusion, and reaction are intimately coupled and can control the catalytic performance. This is particularly true in zeolites. This requires both *ab initio* methods and atomistic simulations and the ability to seamlessly integrate these over different time and length scales. While there is some effort to determine the kinetics of adsorption, reaction, and diffusion, each of these tends to be addressed separately. As such, the solution strategies tend to be ad hoc. The appropriate treatment will likely require the development of new hybrid or coarse-grained methods that can appropriately treat different length and time scales.

As discussed in Chapter 8, Applications of Catalysis: Renewable Fuels and Chemicals, there is an exponential rise in the focus on photocatalysis with response to our future energy challenges. Despite the increase in experimental efforts, the theoretical efforts in photocatalysis have been much more limited. This is due to the challenges of simulating the chemistry of excited states. A rigorous approach to simulating photoexcited states and photocatalysis would require the ability to follow time-dependent processes, and thus the dynamics of intermediates that form, upon a changing excited-state potential energy surface and the cascade of different products. This cannot be solved using traditional static *ab initio* methods, because electron transfer processes and state-to-state transitions are dynamic. While there have been a number of tremendous advances in the application of time-dependent methods such as time-dependent density functional theory, they have been limited to following the reaction dynamics of very small systems (Serrano-Andres and Merchan 2005).

Finally, it is important to note that there has been a significant shift in the emphasis of theory efforts from development to application. There has been an exponential rise in the number of researchers in China and the United States who have recently moved into theory and simulation for catalysis, most of whom have been focused on the use of theory and simulation to examine particular catalytic problems. This is likely linked to the background of the researchers as well as to the nature of funding in the United States and China compared to that in Europe and Japan. The significant increase in the number of scientists in the United States has been in the area of chemical engineering, where the focus has been on solving important catalytic problems. This is driven to some extent by the funding agencies and perhaps by societal views that catalysis (in general) is more of a technology than a fundamental science. Development of theoretical or simulation methods that will significantly enhance our understanding of catalysis are thus only funded when they are tied to the solution of current technological issues such as energy conversion and environmental remediation. While the application of theory is important, there is still a strong need for the method development that will more broadly aid our ability to simulate catalytic systems. This tends to be an issue in the United States as well as China, and it is of growing concern in Europe as well.

EXAMPLES OF APPLICATIONS OF THEORY AND SIMULATION

Computational catalysis has become an important tool in interpreting both spectral and structural information, resolving the reaction intermediates, elucidating the nature of the active site, determining the reaction kinetics, and aiding the design of new materials. Below are highlighted some of the important contributions that theory and simulation have made to the following areas:

- Connecting theory and spectroscopy
- Modeling more realistic reaction environments
- Applications to energy
- Simulating catalytic performance
- Design in heterogeneous catalysis
- From theory to synthesis

Connecting Theory and Spectroscopy

The strongest coupling between theory and experiment has been in the use of theory to predict, interpret, and resolve the structural as well as spectroscopic signatures concerning active surface sites and the nature of the reactive surface intermediates. Theory is being used routinely to simulate infrared, Raman, nuclear magnetic resonance, ultraviolet-visible, X-ray absorption, X-ray photoemission, near-edge absorption fine structure, as well as scanning tunneling and atomic force microscopy in an effort to complement, confirm, and help explain experimental results.

An elegant example of this was shown in the work by Sautet's group (Haubrich et al. 2006 and 2008), which combined extensive density functional theoretical calculations, high-resolution electron energy-loss spectroscopy (HREELS), temperature program desorption spectroscopy, and low-energy electron diffraction in order to identify all of the possible modes of adsorption and the thermal decomposition of prenal

(3-methyl-2-butental), a model α,β unsaturated aldehyde, on Pt and Pt-Sn alloy surfaces. DFT calculations were able to specifically identify the five unique modes of adsorption for prenal (η^2-diσ (CC)-s-trans, η^2-diσ(CC)-s-cis, η^3-diσ(CC)-σ(O)-cis, η^4-diσ (CC)-diσ(CO)-s-trans and η^4-π(CC)-diσ(CO-s-cis) and predict the vibrational frequencies for each of these modes. While the adsorption energies were found to be quite similar for specific surfaces, the simulated HREELS spectra provided a direct fingerprint that could uniquely identify all the modes in the complex experimental HREELS spectra. All five modes of adsorption appear to be present on the Pt(111) surface, demonstrating adsorption energies that range from -47 to -59 kJ/mol. All five adsorption modes along with their adsorption energies are shown in Figure 5.3. A comparison of the computed and experimental HREELS spectrum at 4.9 Langmuir of prenal on Pt(111), given in Figure 5.4, shows the impressive match between theory and experiment.

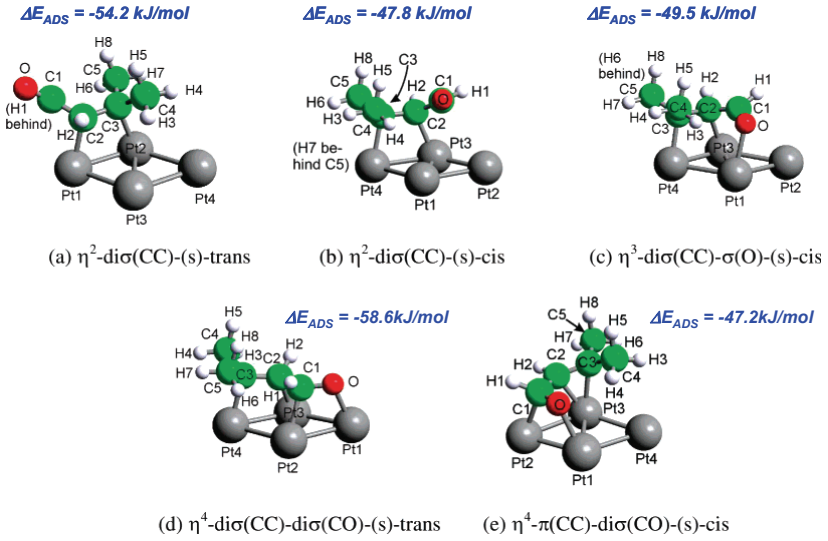

Figure 5.3. DFT-predicted lowest energy adsorption states for prenal (3-methyl-2-butenal) bound to Pt(111) (Haubrich et al. 2008).

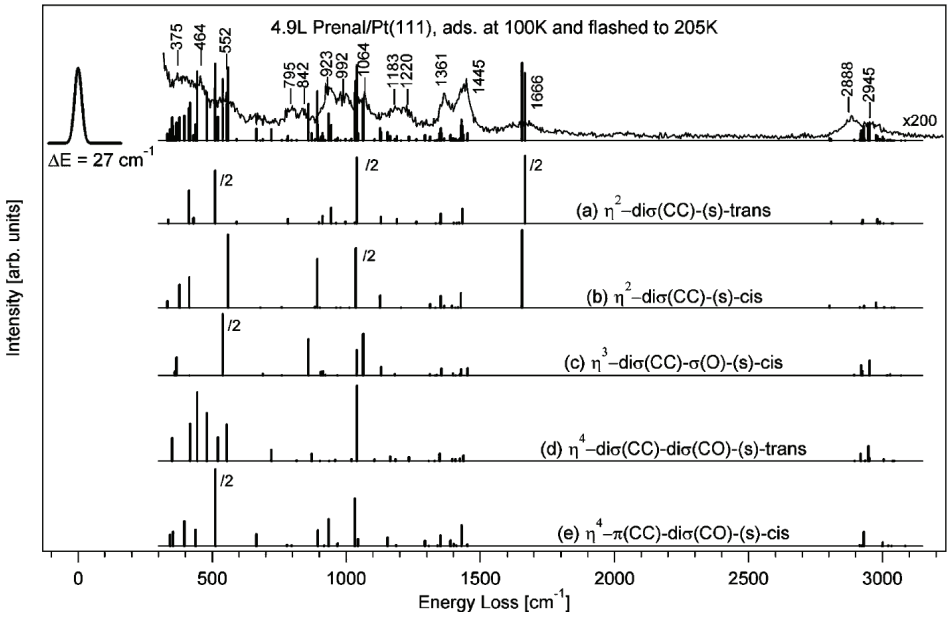

Figure 5.4. Comparison of the experimental and theoretically predicted HREELS spectra for 4.9 Langmuirs of prenal adsorbed onto Pt(111) at 205 K. The HREELS spectra for the five lowest energy adsorption states are given in examples (a)–(e) (Haubrich et al. 2008).

The adsorption of prenal on the Pt-Sn surfaces was found to be significantly different than that on Pt(111), as the adsorption energies were reduced to -39.1 and -30.8 kJ/mol on the Pt_3Sn/Pt(111) surface and -33.4 kJ/mol on the Pt_2Sn surface. The most stable surface adsorption modes for prenal on the Pt_3Sn/Pt(111) surface are shown in Figure 5.5.

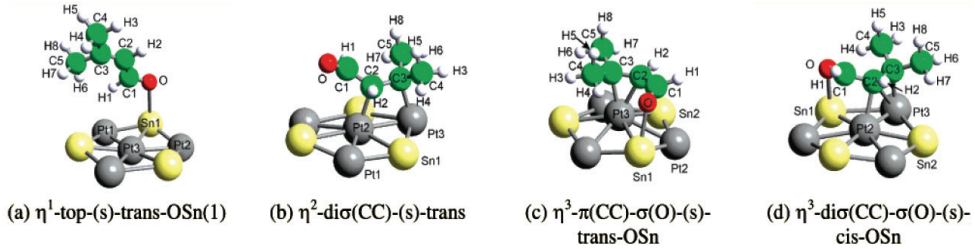

Figure 5.5. DFT predicted lowest energy adsorption states for prenal (3-methyl-2-butenal) bound to Pt_3Sn/Pt(111) (Haubrich et al. 2008).

A comparison of the experimental and theoretical results for the three most stable low-temperature adsorption modes on the $(\sqrt{3}x\sqrt{3})R30°$ Pt_3Sn/Pt(111) surface alloy is shown in Figure 5.6. The results reveal that after annealing the surface to 200 K, only the η^1 mode appears in the HREELS spectra. The predominant adsorption structures that lie parallel to the surface require larger surface ensembles that are not present on the alloy surface. This is noted by the absence of the characteristic vibration frequencies at 375, 956, 1371, and 1444 cm^{-1} in the HREELS spectra. The addition of Sn shuts down the larger Pt ensembles, thus preventing the higher-fold η^2 and η^4 adsorption modes. The interaction between prenal and the surface becomes significantly weaker, as the prenal now adsorbs through its oxygen in an η^1 mode atop of the Sn sites. The results from theory and experiment both show that the addition of Sn leads to a more weakly held prenal intermediate, which binds atop of Sn through its oxygen atom. Theory reveals that there is significant charge transfer from Sn into the neighboring Pt, which shifts the d-band on Pt to lower energies, thus weakening both the Pt-C and the Pt-O interactions. The predominant interaction is then through the Sn-O bond that forms. The overall interaction of prenal with the Pt-Sn surface is thus significantly weaker than the prenal interaction with Pt(111). As such, there is little shift of the vibrational frequencies to those found in the gas phase. DFT, however, cannot readily discriminate between these weak adsorption modes, because they are governed by weak dispersion forces. This begins to push the current limits of theory.

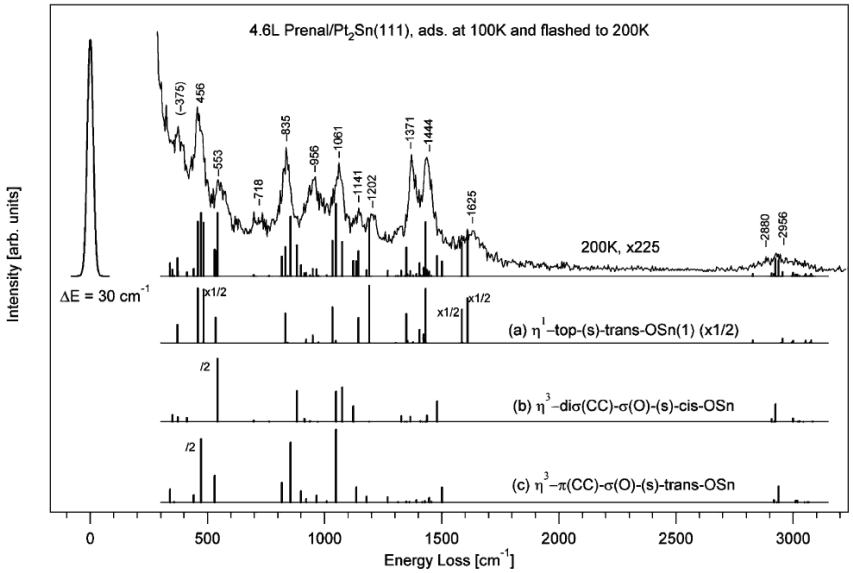

Figure 5.6. Comparison of the experimental and the theoretically predicted HREELS spectra for 4.6 Langmuirs of prenal adsorbed onto Pt_3Sn/Pt(111) at 205 K. The HREELS spectra for the 3 lowest energy adsorption states are given in (a)–(c) (Haubrich et al. 2008).

The results here demonstrate the strong synergy achieved in coupling theory and spectroscopy as they enable complex surface compositions that result from the adsorption of multifunctional molecules on both pure metals and alloys to be resolved at various temperatures. This should enable the resolution of the complex molecular interactions that occur between co-adsorbed molecules under reaction conditions and important information regarding reaction mechanism. It also illustrates that great care must be taken to understand the limits of the theory and where it breaks down.

In addition to the coupling of theory and vibrational spectroscopy, theory is also playing an important role in predicting photoemission and X-ray absorption spectroscopy. Hermann et al. (Hermann et al. 2001; Kolczewski and Hermann 2003 and 2004) have developed an *ab initio* framework by which to simulate angle-resolved, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. A detailed set of *ab initio* calculations were carried out in order to establish the angular dependence of the excitation energies from different final state molecular orbitals along with the dipole transition matrix elements. This information was subsequently used to construct angle-resolved NEXAFS spectra for different electronic states of individual atoms in the surface and help resolve the O 1s excitation for the three different types of oxygen atoms in the V_2O_5(010) surface. The three different coordination environments for oxygen (1-fold, 2-fold, and 3-fold) result in different excitation and absorption spectra that overlap, thus making it difficult, and in some cases impossible, to resolve from experiment alone.

A comparison between the *ab initio* simulated NEXAFS spectra from the $V_{10}O_{31}H_{12}$ model cluster cut from the V_2O_5(010) surface (Figure 5.7) and the experimentally measured V_2O_5(010) surface spectra (Figure 5.8) is shown for both xz polarization and with two different polar angles φ_{pol} = 90° and 20°. The agreement between theory and experiment for the overall spectra is remarkably good. Theory is able to ultimately deconvolute the two major peaks in the spectra into the specific individual excitations from the oxygen states that are responsible. Results reveal that the two peaks at 530 and 535 eV are the result of excitation from the O 1s core electrons to final state orbitals that are comprised of antibonding O 2p and V 3d states. Figure 5.9 shows the orbitals.

The states that appear in the NEXAFS spectra are the result of different local bonding environments and the different oxygen coordination. As such, one can directly assign the two excitation peaks to specific oxygen atoms. The results in Figure 5.8 reveal that for x polarization, both oxygen peaks reveal strong contributions from singly coordinated oxygen atoms, whereas for y polarization the high-energy peak contains contributions from the 3-fold oxygen atoms.

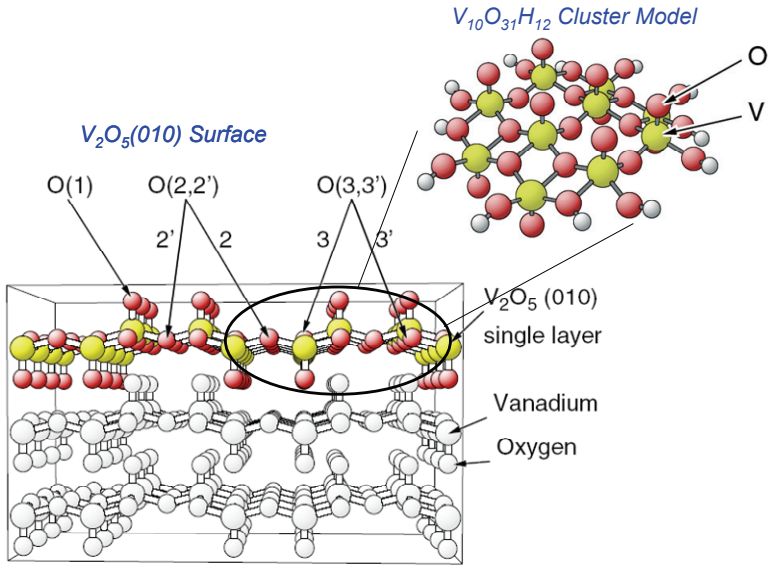

Figure 5.7. Model of the V_2O_5 (010) surface and the $V_{10}O_{31}H_{12}$ cluster model used to calculate the NEXAFS spectra (Kolczewski and Hermann 2003).

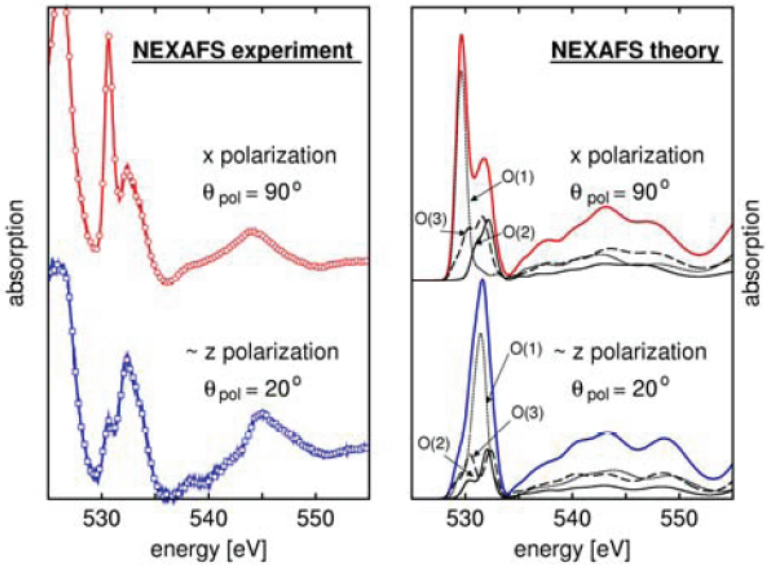

Figure 5.8. Comparison of (*left*) experimental NEXAFS spectra and (*right*) theoretically-predicted O 1s core level excitation spectra for different polarization angles (Kolczewski and Hermann 2003).

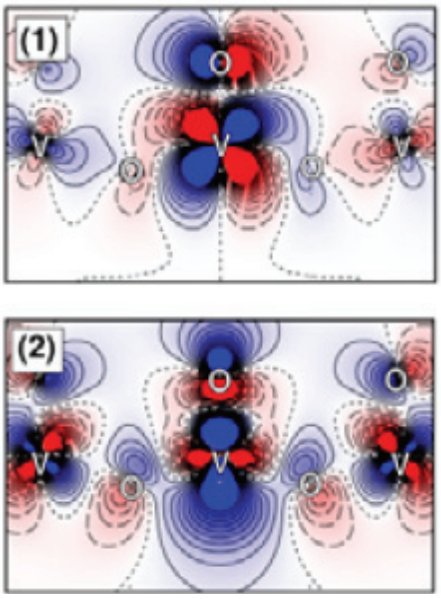

Figure 5.9. Selected final state orbitals for O(1) 1s core excitations (Kolczewski and Hermann 2003).

This combination of theory with experiment should prove to be extremely valuable, because it provides for the direct resolution of the states and the specific structures that give rise to specific X-ray absorption peaks. The interrogation of the surface states before and after adsorption and reaction should enable one to distinguish which of the states are involved in the chemistry and the specific nature of the coordination environment.

The two systems discussed above are just two recent examples of the universal trend in which theory and spectroscopy are being combined to provide unprecedented resolution of the structural features of the catalyst and the surface intermediates under reaction conditions.

Modeling More Realistic Reaction Environments

A second major trend that has taken place over the past few years is the move from the ideal low-coverage single-crystal surfaces to more realistic reaction environments. Simulating the specific conditions that occur *in situ* at the surface of an actual catalyst presents a number of significant challenges, due to the complexity of the environment around the active site. Fully elucidating the reactivity of a supported metal particle, for example, would require an understanding of the metal-support interactions; particle size effects; the influence of alloying; the role of defect sites, promoters, or poisons; and the influence of solution if present. This is shown schematically in Figure 5.10. While we cannot currently model such a complex situation, there has been an increasing number of theoretical and simulation studies aimed at elucidating some of these effects and their importance in catalysis. These results will not only aid in the development of structure-property relationships but also help to establish more coarse-grained models which can mimic these effects. We present two examples which help to highlight the effect of the reaction environment. A more detailed discussion is also given in an example presented later on simulating catalytic performance.

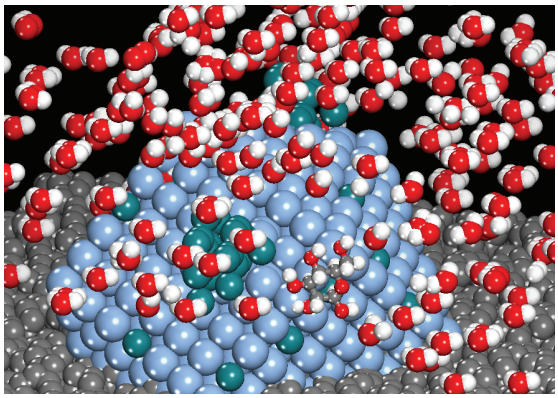

Figure 5.10. Schematic of the complex catalytic reaction environment for a supported bimetallic particle in an aqueous medium.

The increases in computing power that have taken place since 2003 have allowed for the simulation of much larger system sizes to be explored over reasonable time frames. This permits the examination of more extended and realistic features of the reaction environment. In particular, there have been a growing number of studies that have focused on the influence of the support on the activity of metal. This has been fueled in particular by the fascination of the community as to why supported Au nanoparticles are active for a wide range of reactions when bulk gold itself is inactive. The support is thought to play an important role. In order to understand metal-support interactions and their role in catalysis, ultrahigh-vacuum studies have been carried out over nanometer metal particles and layers deposited onto ideal model metal oxide surfaces grown on top of a metal substrate. Previous studies carried out over these supported Au clusters suggest that anionic Au formed as a result of charge transfer from the oxide to the metal is responsible for the unique catalytic activity for the oxidation of CO. Recent combined theoretical and experimental studies by Pacchioni and Freund (Sterrer et al. 2006; Yulikov et al. 2006; Sterrer et al. 2007; Giordano et al. 2008; Ulrich et al. 2008) have shown that the thickness of the oxide films supported on metal substrates plays an important role in the charge transfer properties of the oxide interface that sits between the metal and the support.

Theoretical results from Pacchioni and colleagues (Sterrer et al. 2006; Yulikov et al. 2006) suggest that the charging that occurs may not be associated with the Au/MgO interaction but instead be the result of a charge transfer from the metal substrate through the thin MgO layer and into the Au catalyst particles. They suggested that the thickness of the oxide layer might be ultimately tuned in order to control reactivity. To confirm this, they carried out careful scanning tunneling microscopy (STM) studies of Au and Pd deposited onto 3 ML MgO films supported on Au(001). The STM studies of the surface reveal that Au deposits as single adatoms and order on the thin MgO support with well-defined nearest-neighbor distances, whereas Pd forms a more random dispersion (Yulikov et al. 2006), as shown in Figure 5.11. This indicates that the electronic structure plays an important role in controlling nucleation.

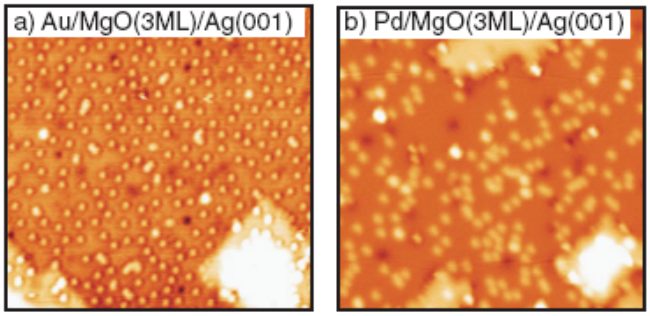

Figure 5.11. STM images for Au (a) and Pd (b) supported on 3 mL of MgO grown on Ag(001) (Sterrer et al. 2007).

Pacchioni and colleagues demonstrate that the ordering of Au on the oxide is the result of repulsive interactions between the Au adatoms on the surface; these repulsive interactions are not present, however, for Pd. Detailed density functional theory calculations using the Tersoff-Hamann approximation for the electronic structure were used to simulate the STM images of neutral and charged Au and Pd atoms on an MgO film (Yulikov et al. 2006). The results were compared with experimental STM images to help resolve the charge states of the metal atoms. The simulation results for anion and the neutral Pd atoms provide a direct match with experiment, as is shown in Figure 5.12. For Au, both the simulation and the experimental STM results reveal a protrusion that is followed by a depression for anionic supported Au adatoms. The results for supported Pd atoms simply show a diffuse protrusion. The "Sombrero" protrusion-depression effect only occurs, however, when Au is charged negatively. Metallic Au displays only a protrusion. In other studies Pacchioni et al. have demonstrated that Au can become anionically charged when it is bound to color centers on the oxide (Sterrer et al. 2006); Au bound to terraces remained neutral. The adsorption of CO onto the anionic supported Au provides a clear fingerprint in the CO vibrational stretching frequencies by which one can analyze the influence of the support.

The results here show the important synergy between theory and experiment and help to demonstrate that the charge transfer that exists between the metal and the support is a function of the oxide layer thickness as well as a function of the nature of the supported metal.

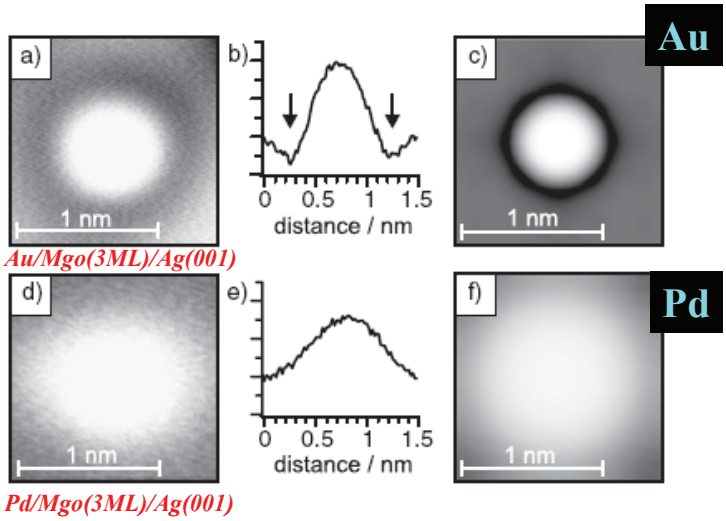

Figure 5.12. Comparison of experimental STM images for Au (a) and Pd (d) atoms supported on 3 mL MgO films on Ag(001) with DFT-simulated images for Au (c) and Pd(f) on 3 mL MgO supported on Ag(001). The experimental height profiles on Au and Pd are given in b and e, respectively (Sterrer et al. 2007).

In addition to the support, the effect of the gas phase conditions at the active site can also be important in controlling the site's activity and selectivity. The gas phase pressures and the surface kinetics ultimately control the surface coverages, which in turn dictate the rates of reaction. Scheffler and colleagues developed a novel first-principles approach to determining the thermodynamically preferred surfaces at different conditions (Scheffler 1988; Reuter and Scheffler 2002; Stampfl et al. 2002; Reuter and Scheffler 2003b). This approach has now become the accepted standard in establishing the thermodynamically favored surface compositions for metals, metal oxide, and metal sulfide surfaces. The calculation of free energies for different surface structures are used together with the chemical potentials for the gas phase intermediates to calculate the lowest free energy surface states that can form at specific partial pressures and temperatures.

Raybaud et al. (Arrouvel et al. 2005; Costa et al. 2007; Raybaud 2007; Raybaud et al. 2008) extended the idea to understanding the surface composition and the potential reactivity of metal sulfide particles and their interaction with different supports. More specifically, they examined the metal-sulfide particle formation on both an anatase TiO_2 and a γ-alumina support (Costa et al. 2007). The partial pressures of water, hydrogen, and H_2S at different temperatures were used together with DFT-calculated surface free energies to determine the hydroxylation and sulfidation state of the support under different reaction conditions (Arrouvel et al. 2005; Costa et al. 2007; Raybaud 2007; Raybaud et al. 2008). DFT calculations on the Mo and sulfur edges of the different MoS_2 and CoMoS surfaces were used to understand the reactivity of these supported surfaces and particles. The surface phase diagrams for Mo_6S_x clusters on γ-alumina and anatase TiO_2(101) surfaces are shown in Figure 5.13.

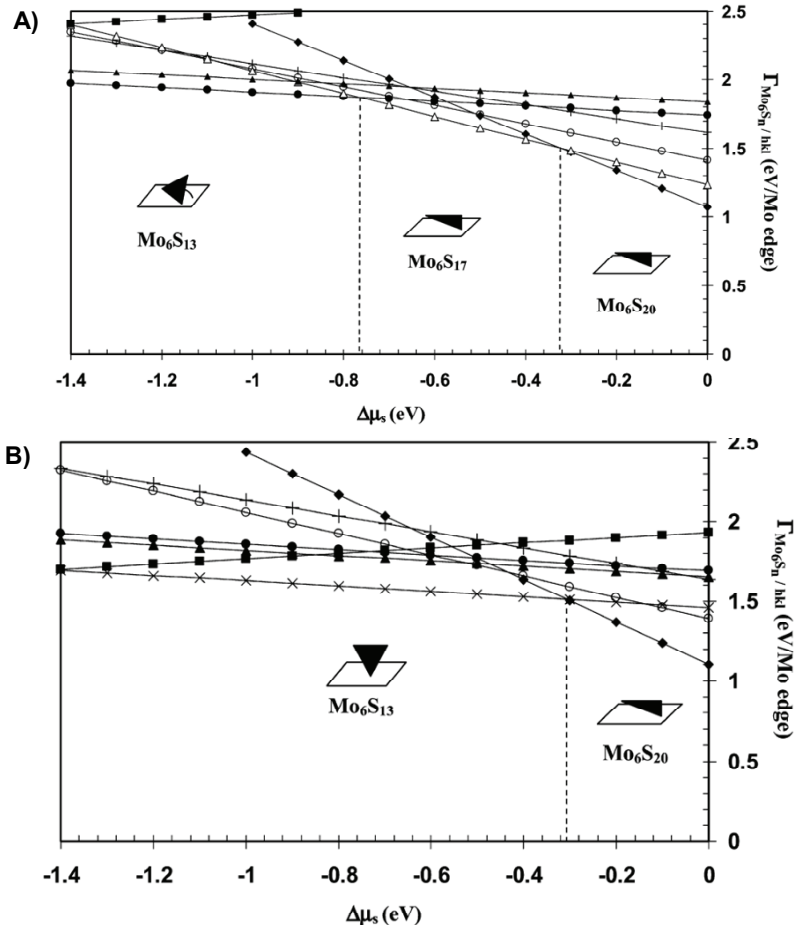

Figure 5.13. DFT-calculated surface phase diagrams for Mo_6S_{13}, Mo_6S_{17}, Mo_6S_{20} clusters supported on (A) gamma-Al_2O_3 (100) and (B) anatase TiO_2(101) (Costa et al. 2007).

The results reveal characteristically different wetting behavior for MoS_2 clusters supported on anatase TiO_2 than those on γ-alumina. The MoS_2 clusters prefer epitaxial growth on anatase TiO_2, which leads to the formation of tilted structures with respect to the support, and therefore, to poor wetting of the support. These same clusters on the γ-alumina resulted in much better wetting of the support. The surface free energies of the S-edge and the Mo-edge of the particles anchored to TiO_2 and γ-alumina were subsequently used together with a Gibbs-Curie-Wulff-Kaischew method to determine the geometric parameters of the supported MoS_2 clusters (Costa et al. 2007). The resulting proportion of free Mo and S edge sites as a function of the particle diameter on both anatase TiO_2 and γ-alumina is shown in Figure 5.14. The average particle size for MoS_2 on TiO_2 is about 38 Å, whereas that on γ-alumina is higher at 49 Å.

The results in Figure 5.14 would then suggest that there are a similar number of free edge sites. The relative percentage of S/Mo edge sites however was found to be higher for γ-alumina. There is a loss of S-edges on anatase due to edge wetting of the support. In addition, there appears to be a stabilization of particles with higher vacancies on the TiO_2 support. As a result, the higher intrinsic activity for HDS on anatase over γ-alumina is due to these differences in the nature of the exposed edge sites.

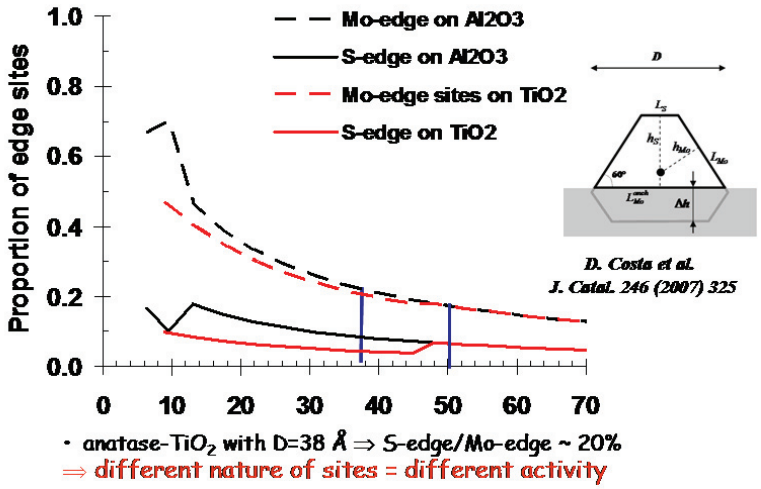

Figure 5.14. Distribution of sulfur and molybdenum edge sites as a function of MoS_2 particle diameter supported on γ-alumina and TiO_2 anatase substrates (Costa et al. 2007).

Recent advances in embedding methods have allowed for the resolution of structure and reactivity in complex micro- and mesoporous materials. The region about the active site is treated quantum-mechanically, whereas the effects of the porous framework are treated with lower-level QM or molecular mechanics (MM) models. Malek, Li, and van Santen (Malek, Li, and van Santen 2007; Zhang et al. 2008), for example, used a DFT/MM embedding approach to follow the potential energy surface for the enantioselective epoxidation of cis- and trans- methyl styrene by an oxo-Mn-V-salen complex anchored into the channels of MCM 41.

The optimized structure of the anchored complex is shown in Figure 5.15. Both electronic and steric confinement effects were found to cooperatively control the reactivity and enantioselective behavior of this material. The triplet state potential energy surface for the oxygen transfer reaction to the adsorbed trans-methyl styrene molecule is shown in Figure 5.16. Even though trans-methylstyrene was found to have the greatest asymmetric induction effect, the cis form resulted in the lowest activation barriers. The immobilization by the electron-donating linker used to anchor the complex was found to decrease the barriers. In addition, the channel structure was also found to reduce the activation barriers and enhance enantioselectivity as the result of the confinement and distortion of the Mn-salen complex. Channel confinement was therefore found to greatly depend upon the channel size.

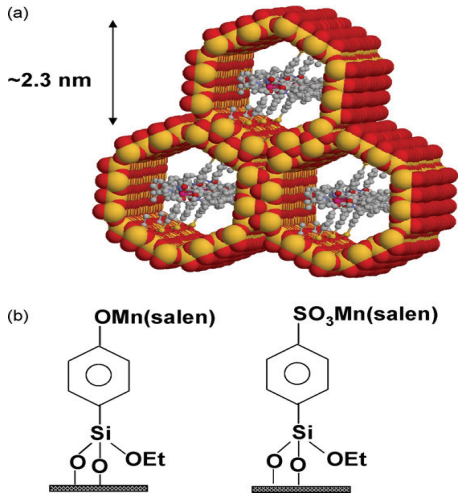

Figure 5.15. Mn-salen complexes anchored inside the channels of MCM-41 and the explicit anchors used in the DFT calculations (Malek, Li, and van Santen 2007).

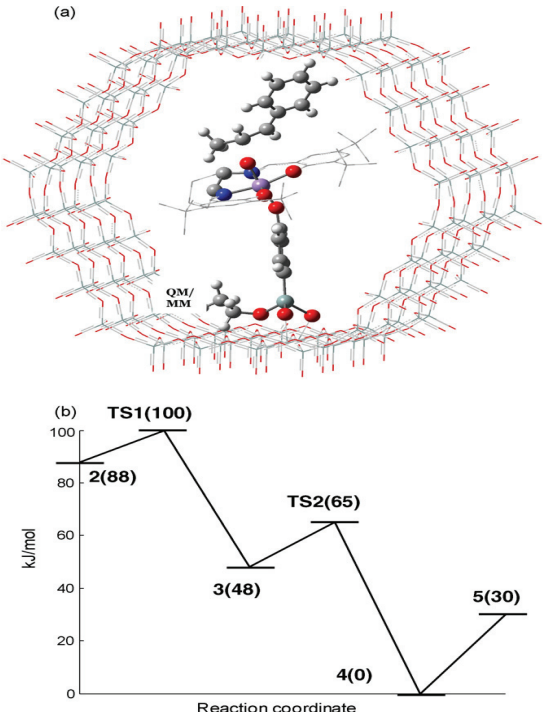

Figure 5.16. (a) The DFT/MM optimized adsorbed methylstyrene onto the Mn-salen complex anchored inside the MCM-41 channel; (b) the reaction energy diagram for the oxygen transfer reaction along the triplet energy surface (Malek, Li, and van Santen 2007).

Applications to Energy

The application of theory and simulation to catalysis has covered a broad range of different applications, including NO_x reduction, selective oxidation, selective/enantioselective hydrogenation, dehydrogenation, catalytic cracking, isomerization, reforming, desulfurization, and dechlorination. The recent trends, however, reveal an increasing focus on the application to energy. This includes work in the following areas:

- Methane conversion
- Fischer Tropsch synthesis
- Electrocatalysis
- Photocatalysis (just emerging)
- Coal conversion (just emerging)
- Biorenewables (just emerging)

Most of the energy efforts are related to the more traditional processes such as methane conversion routes and Fischer Tropsch (FT) synthesis. This is due to the fact that the initial reactants for methane conversion and FT, namely CH_4 and CO/H_2, are small molecules for which there is considerable experimental data and previous theoretical results on well-defined surfaces. Electrocatalysis is an area that has witnessed tremendous growth since about 2002. The challenges of modeling the complex electrocatalytic reaction environment present in a proton-exchange membrane fuel cell, however, have severely limited most modeling efforts. A rigorous description of the reaction environment requires simulating the metal, carbon support, polymer electrolyte, solution phase, and constant electrochemical potential. Despite this complexity, there have been a number of initial successes in modeling electrocatalysis using simple models of the surface and the solution. These initial successes as well as the importance of fuel cells have stimulated a strong and recent interest in modeling these systems. The small size of the molecules of interest (CO, H_2, O_2, H_2O, CH_3OH, HCOOH, etc.) also helps to make electrocatalysis more attractive for theoretical studies.

There is also a growing interest in modeling other more complicated systems such as photocatalysis, coal conversion, and biorenewables. There is a concerted effort in Japan, for example, to model photocatalysis, and China has strong efforts in coal conversion. Despite the interest, the complexity of the reaction environment in all three of these areas has significantly inhibited progress; all three areas, however, will likely see considerable future growth for modeling in Asia, Europe, and the United States.

Simulating Catalytic Performance

While theory can be used to determine the elementary reaction steps involved in a catalytic system, the activation barriers for each step and the influence of the reaction environment, it cannot provide catalytic performance or kinetics directly. Catalytic activity and selectivity require simulating the rates of reaction, which are inherently dependent upon the rate constants as well as the surface coverages under working conditions. This can be carried out either via the development of microkinetic models or through the use of kinetic Monte Carlo simulations, as discussed earlier. A nice example of the latter was presented by Reuter and Scheffler, who combined *ab initio* calculations with rigorous statistical mechanics and integrated the results into kinetic Monte Carlo simulations to follow the oxidation of CO over the $RuO_2(110)$ surface (Reuter and Scheffler 2002; Reuter and Scheffler 2003a; Reuter and Scheffler 2003b; Reuter, Frenkel, and Scheffler 2004; Reuter and Scheffler 2006).

A rigorous set of DFT calculations was used together with the chemical potentials for oxygen and Ru to determine the free energies for different terminations of the $RuO_2(110)$ surface as a function of the temperature and the partial pressures of oxygen and CO. The resulting surfaces that can form and their free energies are plotted with respect to the partial pressure of oxygen in Figure 5.17. These surfaces are comprised of Ru and oxygen centers. Oxygen and CO can adsorb at either the bridge (br) or the coordinatively unsaturated Ru sites (cus), referred to as O_{br} and O_{cus} and CO_{br} and CO_{cus}, respectively.

Density functional theory results reveal that as the partial pressure of oxygen is increased, the most stable surfaces shift from CO_{br}/CO_{cus} coverages at low oxygen partial pressures to O_{br}/CO_{cus} coverages at moderate pressures, and then to O_{br}/O_{cus} coverages at very high oxygen partial pressures, which might be expected as oxygen begins to compete for both the O_{br} and O_{cus} sites. The results were subsequently used to map out a thermodynamic phase diagram for the different states of oxygen and CO as a function of the partial pressures of CO and O_2, as well as the reaction temperature. The activation barriers for the CO oxidation at different sites and O_2 desorption were also calculated and used together with transition state theory to determine the rate constants. The detailed reaction PES for the reaction of $CO_{cus} + O_{cus}$ is shown in Figure 5.18.

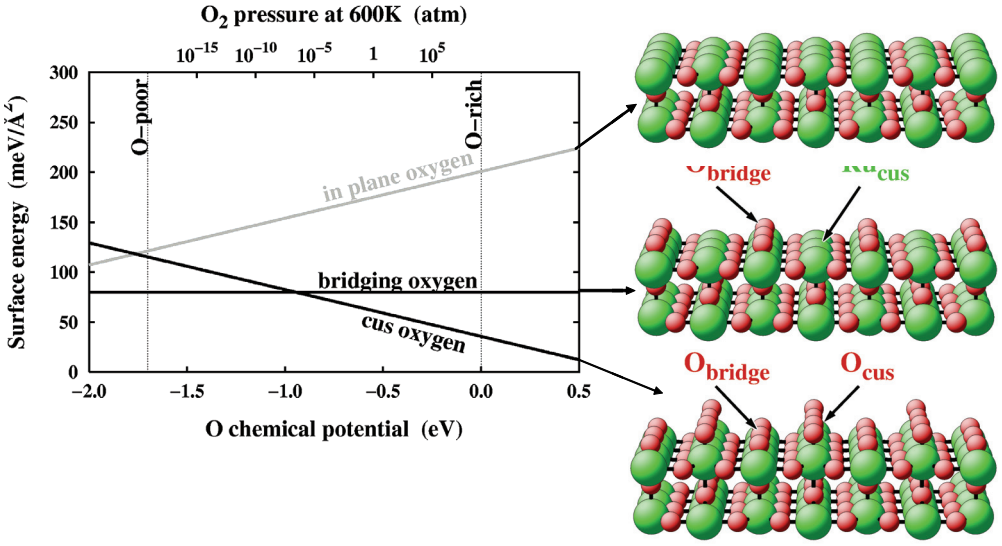

Figure 5.17. DFT-derived phase diagram for oxygen on $RuO_2\{110\}$. The surface free energies for the in-plane oxygen, O_{br}/Ru_{cus} and O_{br}/O_{cus} terminated surfaces as a function of the chemical potential (and partial pressure) of oxygen at 600 K (Reuter and Scheffler 2003b).

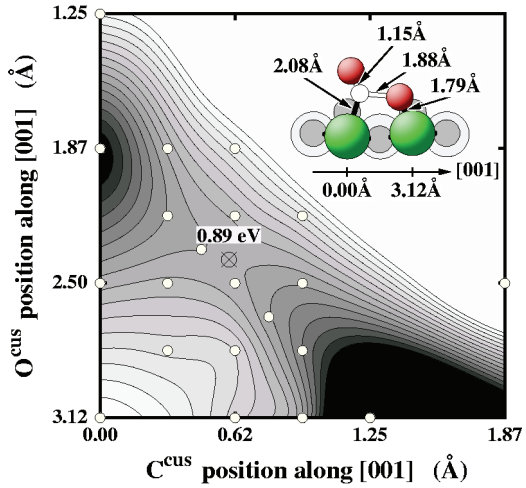

Figure 5.18. DFT-calculated potential energy surface for the reaction of $CO_{cus} + O_{cus}$ on $RuO_2\{110\}$ to form CO_2 (Reuter and Scheffler 2003a and b).

The resulting *ab initio*-derived thermodynamic results along with the activation barriers were subsequently used as input to a kinetic Monte Carlo simulation to follow the temporal behavior for CO oxidation over the surface for a range of different reaction conditions. This allowed for the simulation of reaction rates from ultrahigh vacuum (UHV) conditions on up to high pressures of CO and O_2 and temperatures relevant to the actual catalytic conditions. The simulations provide a detailed understanding of the surface coverages, the rates, and the elementary steps that control the reaction at different conditions. At low partial pressures of CO, the simulations reveal that all of the coordinatively unsaturated Ru surface sites are covered with oxygen; CO is therefore blocked from the surface, which severely inhibits the rate. As the pressure of CO is increased up to about 20 atmospheres, the rate is considerably enhanced. Snapshots from the simulation reveal that CO is bound to the cus sites, whereas oxygen is predominantly located on the bridge sites. There is some mixing, though, as the fractional occupation of different sites at a particular point in time was found to be $N_{CO(br)}$=0.11, $N_{CO(cus)}$ = 0.7, $N_{O(br)}$=0.89, and $N_{O(cus)}$=0.29. The predominant reaction path to CO_2 involves the reaction $CO_{cus} + O_{cus}$ -> CO_2. The reactions $CO_{br}+O_{cus}$ -> CO_2 and $CO_{cus} + O_{br}$ ->CO_2 still occur

but are less favorable. An analysis of these paths demonstrates that an optimal balance is required between the lower activation barriers for the $CO_{br} + O_{cus}$ and the higher coverages of CO_{cus} and O_{br}. The results reveal the important message that a strict analysis of the activation barriers or the thermodynamics alone leads to incorrect conclusions on the steps that govern the kinetics. The accurate determination of the reaction rate thus requires the full kinetic simulation of all of the reaction steps, because they ultimately control the surface coverage as well as the reaction rate.

The highest CO_2 formation rates were found for systems with optimal CO and O_2 partial pressures that would result in surface compositions that lie within the very narrow region of the surface phase diagram where the CO_{br}/CO_{cus} and O_{br}/O_{cus} interfaces meet, as is seen in Figure 5.19. The dark regions in the right side of Figure 5.19 are those that have the highest activity. The simulation results were found to be in very good agreement with previously reported experimental results for CO oxidation over a range of different partial pressures of CO and O_2 as is shown in Figure 5.20 (Reuter and Scheffler 2006). There has been some debate, however, as to whether the active surface is an oxide or a highly covered metal (Goodman et al. 2007).

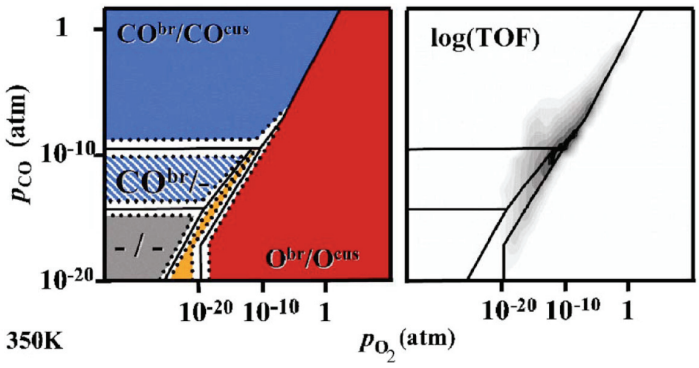

Figure 5.19. First-principles DFT-based kinetic Monte Carlo simulation results for (*left*) the steady state surface structures of the $RuO_2(110)$ surface, and (*right*) CO oxidation turnover frequencies over the $RuO_2(110)$ surface as a function of the partial pressures of CO and oxygen at a temperature of 350 K (Reuter and Scheffler 2006).

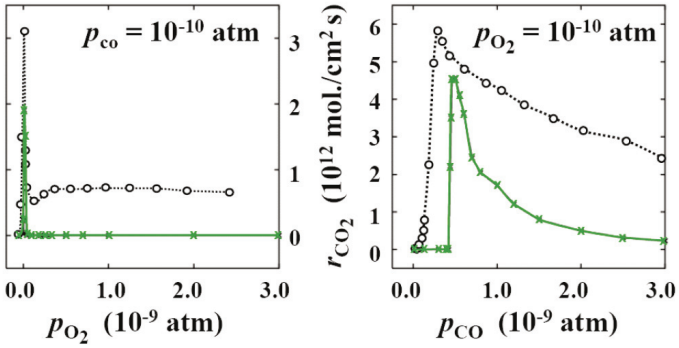

Figure 5.20. Comparison of the first principle DFT based kinetic Monte Carlo simulation with experiments for the rate of CO_2 formation over RuO_2 at 350 K (Reuter et al. 2004).

The message here is not so much whether one can discriminate between the metal and oxide surfaces but instead the fact that the true understanding of catalysis requires a full consideration of the kinetics under working conditions and the influence of the appropriate steady state surface coverages. This was just one example of moving from a pure quantum mechanical treatment to simulating the actual kinetics under reaction conditions. While the simulation of kinetics is of critical importance to catalysis, there are still relatively few practitioners who attempt to connect *ab initio* results to reaction rates at appropriate conditions. Understanding the kinetics under working conditions will become even more important as the community shifts to more complex reaction systems.

Design in Heterogeneous Catalysis

In addition to the prediction of properties and the elucidation of mechanism, theory and simulation are beginning to be used to aid in the design of novel nanoscale catalytic materials. One of the key findings from the 2002 WTEC study on Applying Molecular and Materials Modeling (Westmoreland et al. 2002) was the degree to which industry had used modeling to aid in homogeneous catalyst discovery and to protect intellectual property. There were very few efforts, if any, at the time aimed at guiding the design of heterogeneous catalytic systems. The complexity of heterogeneous catalytic systems was thought to be too great a challenge. Advances in modeling and detailed characterization over the past decade, however, have significantly increased our understanding of catalysis and have provided the basis for the emergence of various studies aimed at the design of new catalytic materials.

Most of the efforts to date have focused on the development of catalytic "descriptors" that can be used to predict experimental trends. This is analogous to the quantitative-structure-activity relationships used in drug design. One of the key differences, however, is that the electronic and structural descriptors used in drug design do not appear to work in predicting catalytic behavior. The development of "descriptors" that correlate the bulk behavior of metals, metal oxides, and metal sulfides with their reactivity has not been very successful. This may be due to the complexity of catalytic systems or due to the fact that bulk properties are not representative descriptors of the surface properties. More realistic descriptors might focus on properties that are tied to the actual bond-breaking and bond-making events that occur at the surface. Many of these steps appear to be governed by the strength of the adsorbate-surface bond. While this has been recognized for some time, it has only recently been used in order to screen catalytic materials as the increases in computational power now make it possible to readily examine a range of different materials.

This was elegantly demonstrated by the Nørskov group, which showed through detailed DFT calculations and a rigorous kinetic analysis that the optimal catalyst for the methanation reaction

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

would have an optimal CO dissociation energy (Andersson et al. 2006). This falls out of a Sabatier analysis that indicates the optimal material will facilitate the dissociation of CO yet still allow for both the carbon and the oxygen atoms that form to be hydrogenated on the surface. This is confirmed from DFT results for the elementary steps involved in the hydrogenation of CO to methane. As a result, the catalytic activity should follow the classic volcano shaped curve as a function of the calculated dissociation energies, as is shown in Figure 5.21. The lines in Figure 5.21 represent the best fit to the data. The optimal dissociation energy (ΔE_{diss}) appears to be 0.06 eV.

While Ni is used commercially, the results from the volcano curve in Figure 5.21 (bottom) reveal that Ru and Co are more active than Ni. Ru, however, is much more expensive than Ni. It is clear that the optimal material may need to satisfy more than a single design criterion, thus requiring the solution of a multi-objective optimization problem. Nørskov and colleagues used a Pareto-optimal set to guide their search for active low cost materials (Andersson et al. 2006). *Ab initio* DFT calculations were thus carried out together with a simple alloy interpolation model in order to screen 117 different alloys in the search for other likely alloy candidate materials. A Pareto plot of the results comparing the cost against the activity is shown in Figure 5.22. The best materials should be cheap and have a value for ΔE_{diss} as close to 0.06 eV as possible. The results show that while Fe is the cheapest material, its activity, as measured by the descriptor $\Delta E_{diss,}$ is not as good as Ni, Rh, Co, or Ru.

On the other hand, the costs of Ru and Rh are significantly higher than Ni, Co, and Fe. The optimal alloys are those that lie at "knee" in the bottom left of the Pareto plot, namely the $FeNi_3$ and NiFe alloys, because they have descriptors near optimal activity and are relatively low in cost. A class of different NiFe alloys was subsequently synthesized experimentally and tested (Kustov et al. 2007). The results nicely confirmed the theoretical predictions, which indicate that the Ni_3Fe and NiFe alloys have activities that mimic those of Co but are significantly cheaper than Co.

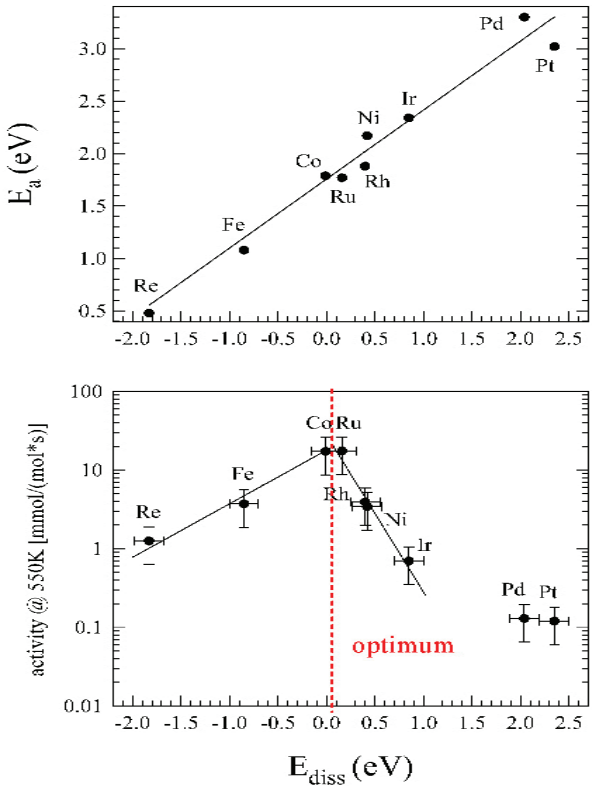

Figure 5.21. The choice of an appropriate reactivity descriptor for the catalytic methanation reaction. (*Top*) The Brønsted-Evans-Polanyi relationship linearly relates the CO activation energy with the CO dissociation energy. (*Bottom*) CO activation over different metals shows a characteristic Sabatier principle with an optimum C-O bond dissociation energy (Andersson et al. 2006).

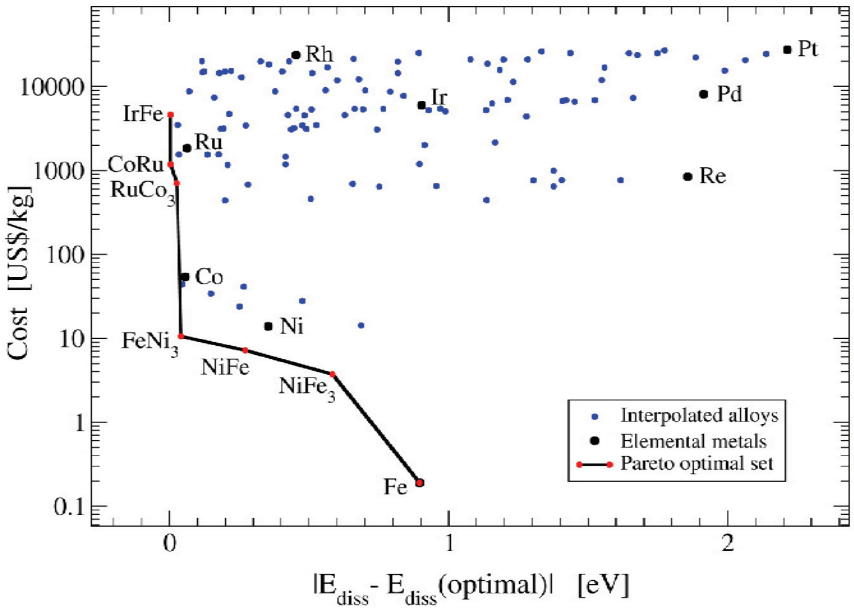

Figure 5.22. The Pareto-optimal search for improved methanation catalysts. The optimal material should have the highest activity as measured here by the CO dissociation energy predictor along with the lowest cost. The best materials sit in the bottom left hand corner of the curve (Andersson et al. 2006).

The authors have used similar approaches to identify novel catalytic alloy materials for ammonia synthesis (Jacobsen et al. 2001; Logadottir and Nørskov 2003; Bligaard et al. 2004; Boisen et al. 2005; Honkala et al. 2005; Hellman, Baerends, et al. 2006; Hellman, Honkala, et al. 2006) and, recently, acetylene hydrogenation (Studt et al. 2008). They conclude that the predictive power of DFT is attributed to the fact that the width of the volcano curve is large enough to overcome any systematic errors in calculating reaction energies. These are just few examples of the emerging trend of using theory to determine appropriate descriptors that can subsequently be used to screen different materials in the search of optimal catalysts.

From Theory to Synthesis

One of the key conclusions from a 2003 NSF workshop report *Future Directions in Catalysis: Structures that Function on the Nanoscale* (Davis and Tilley 2003) was the need for theory and simulation methodologies to provide: "… deeper understanding and more complete descriptions of complex reactions and collective behavior including self-assembly in solution." It was recognized that simulating catalyst synthesis presents a tremendous but important challenge for theory and simulation, because these processes are controlled by ill-defined wet chemical laboratory methods. Despite its importance, little has been done in the area of synthesis. This is due to the complexity of modeling collective solution phase processes that govern synthesis, such as nucleation, precipitation, and growth. In the present assessment, all of the work that the WTEC panelists saw was focused on moving from structure to function rather than from synthesis to structure. There are, however, a few efforts in the literature that should be mentioned that have been aimed at the design of zeolite templates and their role in controlling the zeolite morphology.

Early efforts by Catlow and Thomas (Lewis, Freeman, and Catlow et al. 1995; Lewis et al. 1996; Willock et al. 1997; Catlow, Coombes, and Pereira 1998) demonstrated how molecular-level simulations could be used to design template molecules to help direct the synthesis of specific zeolite frameworks. The templates are generally organic bases that are added during synthesis to control the crystallization of the porous framework structure around them. Simulations were thus used to "grow" the optimal template molecule inside a particular zeolite so as to optimize the interactions between the molecule and the pore. In this work, a new code termed ZEBEDDE (Zeolites by Evolutional Denovo Design) was developed and used to carry out the following functions: (1) molecular building, (2) rotate, (3) shake and (4) rocking functions, as well as (5) bond twist, (6) ring formation, and (7) energy minimization in order to grow the molecule within the framework (Lewis et al. 1996). This was demonstrated with the design of the 4-piperidiopiperidene template molecule to aid in the synthesis of the levyne zeolite structure. The intermediates generated in the "growth" process, starting with methane, are shown in Figure 5.23, along with the fit of the final 4 piperinopiperidene template within the levyne structure. While this work initially generated much excitement, there have been only a few subsequent papers in the area (Barrett et al. 1996; Lewis, Catlow, and Thomas 1997; Lewis et al. 1997).

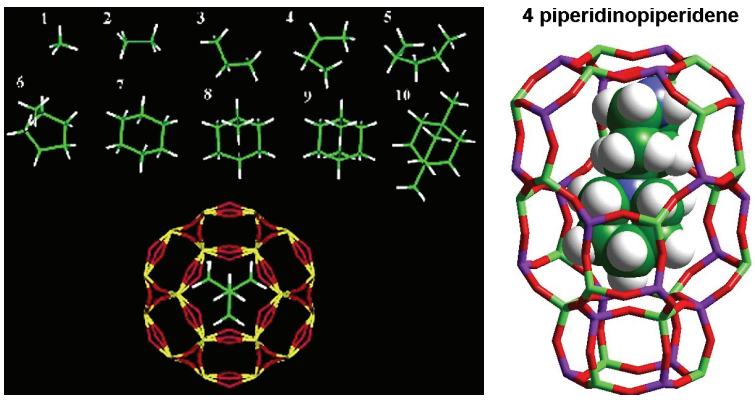

Figure 5.23. The 4-piperidiopiperidene template molecule was established by using a *de novo* design strategy where atomistic simulations were used to "grow" the optimum molecule within the zeolite cage. The simulations start with methane shown in number 1 above (*top-left*) and sequentially "grow" the template molecule within the microporous levyne structure via a sequence of different steps, including (1) build, (2) rotate, (3) shake, (4) rock, (5) bond twist, (6) ring formation, and (7) energy minimization (Lewis et al. 1996).

A more recent study by Burton and Zones (Zones and Burton 2005; Burton 2007) used molecular simulations to determine the structure-directing influences of small amines in the crystallization of the MTT–zeolite phases. They predicted various novel amines and quaternary ammonium molecules with isopropyl, dimethylamino, tert-butyl, and trimethylamimonium groups connected via methylene spacers at 5 Å or multiples of 5 Å intervals that are able to crystallize the target MTT phases. The 5 Å spacers were found to be critical in the selective synthesis of specific phases. The molecules provide an optimal fit inside the MTT pores.

SUMMARY AND FUTURE DIRECTIONS

The close integration between theory and simulation with experiment has proven to be invaluable in establishing new insights into the structure and reactivity for a broad range of different catalytic materials and catalytic reactions. Theory has been instrumental in interpreting and resolving spectral data derived from infrared and Raman, ultraviolet, X-ray photoemission, near-edge absorption fine structure, nuclear magnetic resonance, scanning tunneling, temperature programmed desorption, and reaction studies. This synergistic combination of theory with spectroscopy has provided a wealth of information about the nature of the active site and the reactive intermediates for different catalytic systems. This detailed integration of theory and spectroscopy will undoubtedly continue and strengthen in the future with the advances in theory and characterization.

In addition to the advances in the prediction of structure and spectroscopy, theory and simulation have proven to be invaluable in the determination of complex potential energy surfaces and the corresponding kinetics for different surface processes. This has allowed for the elucidation of the elementary reaction steps, the influence of the reaction environment, and the resolution of rigorous catalytic kinetic studies. Future computational developments will expand the system sizes that can be simulated and thus significantly enhance our ability to elucidate the active site and the influence of its nanoscale environment (i.e., support, surface coverage, surface composition and structure, solution, applied potentials) on the intrinsic catalytic chemistry and kinetics, as well as on overall catalytic performance.

In just the past few years, theory and simulation have also emerged as valuable tools in establishing structure-reactivity relationships and aiding in the design of new materials. It is expected that both of these areas will increase significantly in the coming years. There will likely be more efforts focused not only on catalyst behavior but also on coarse-graining the surface simulations to detailed reactor models in an effort to link both catalyst design and optimal reactor performance.

In addition to the intrinsic catalytic activity and selectivity discussed, there are a number of other important practical issues that will likely drive both applications and the development of new methods in theory and simulations. These include catalyst

- Synthesis
- Stability
- Deactivation
- Durability

All four of these are critical engineering considerations that will require the ability to simulate disparate changes in both length and time scales in order to bridge the atomic and molecular processes that govern these features to actual macroscopic behavior.

Theory and simulation have been used to examine a wide range of important applications, including fine chemical synthesis, NO_x reduction, selective oxidation, methanol and Fischer-Tropsch synthesis, chemo- and entioselective hydrogenation, electrocatalysis, alkylation, reforming, combustion, etc. It is very likely that most of the future applications will involve efforts in renewable energy: it is expected that there will be significant efforts in photocatalysis, electrocatalysis for fuel cells, and the conversion of biorenewable resources.

The significant advances in *ab initio* quantum mechanical methods, computational architectures, and computational power that have occurred over the past two decades are at the heart of the unprecedented advances in modeling catalytic systems. Despite these advances, improvements in method accuracy increase slowly. There are, however, major efforts in the theoretical chemistry and physics communities, which are aimed at the development of faster and more accurate methods to simulate complex materials. These include order-N scaling methods that can regularly simulate thousands of heavy atoms; more accurate DFT functionals, many body techniques, and quantum Monte Carlo methods that will offer significantly improved energies, band gaps, and electronic properties; improved parallelization schemes that will enable significant increases in system sizes; more robust transition-state search methods that will allow for rapid isolation of transition states; solid-state time-dependent DFT methods that will allow for a more accurate treatment of excited states and photocatalysis; and constant potential *ab initio* methods to simulate electrocatalytic systems.

The ability to simulate more complex issues such as catalyst synthesis, catalyst stability and durability, as well as photocatalysis and the conversion of renewable feedstocks will require the development of accurate coarse-grained models that enable the coupling between the electronic, atomic, nano, micro, and mesoscopic time and length scales. This will require further advances in robust force fields that can accurately treat reactive systems without heroic parameterization efforts, reactive molecular dynamics simulations, and "smart" kinetic Monte Carlo simulations that can accurately estimate internally within the simulation the activation barriers for the myriad of different reaction steps.

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CHAPTER 6

APPLICATIONS: ENERGY FROM FOSSIL RESOURCES

Levi Thompson

INTRODUCTION

Fossil resources, including petroleum, natural gas, and coal, presently account for nearly 85% of all the energy consumed in the world (EIA 2008; Figure 6.1) and the emission of nearly 30 billion tons of CO_2 annually (IPCC 2007). The United States accounts for approximately 20% both of total energy resources consumed and CO_2 emitted (Figure 6.2) worldwide. With energy consumption predicted to double in the next 50 years and fossil fuels expected to satisfy much of this demand, there is growing interest in improved processes and materials to convert these fossil resources into fuels and remediate the CO_2 and other greenhouse gases emitted during combustion. Catalysts and catalytic processes will play key roles in both areas.

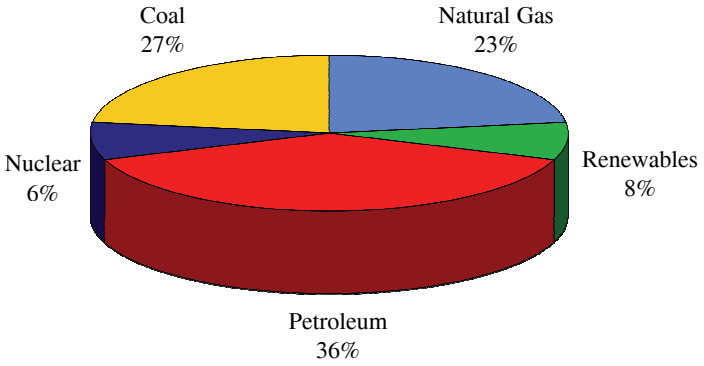

Figure 6.1. According to the U.S. Energy Information Administration, 482.5 quadrillion BTUs of energy were consumed globally in 2007, with more than 86% coming from fossil resources. This represents an increase of 21% from the 2000 consumption rate (statistics, EIA 2008).

This chapter examines research and development activities related to the conversion of fossil resources, with an emphasis on catalysis for the production of liquid transportation fuels and hydrogen, and for emission control including the reduction of CO_2. Efforts in these areas span significant length and size scales, with work in Asia focusing on practical catalysts and processes with large-scale demonstration efforts, and work in Europe focusing on more fundamental investigations of catalyst function and the discovery of new formulations and processes. The following sections provide snapshots of information shared with the WTEC delegation of U.S. engineers and scientists during visits to key institutions in Asia and Europe. In some cases findings from the site visits are supplemented with information from the literature.

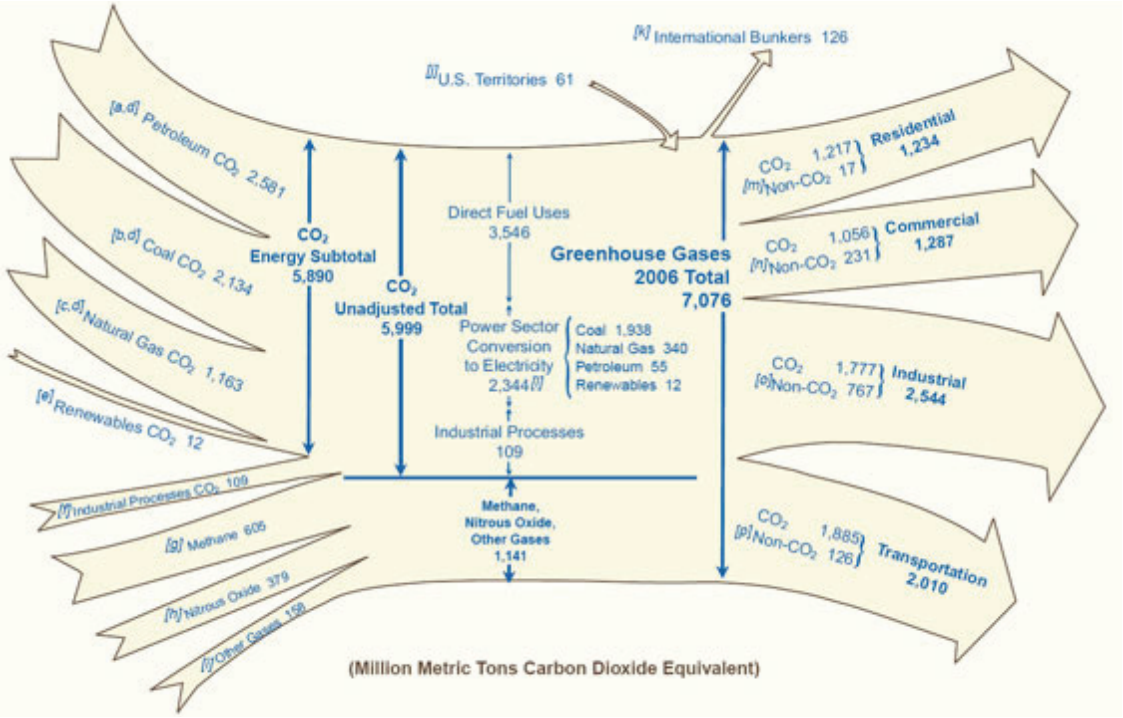

Figure 6.2. Carbon dioxide emission flow chart illustrating amounts and sources for the United States in 2006 (EIA 2007).

PRODUCTION OF LIQUID FUELS

Catalysts for Petroleum Refining

Nearly 95% of all liquid transportation fuels are produced from petroleum. The refining of petroleum into gasoline, diesel, jet fuels, and other transportation fuels involves a fairly complex network of processes. The key catalytic processes are catalytic reforming, hydrotreating (e.g., hydrodesulfurization and hydrodenitrogenation), and catalytic cracking (Figure 6.3). Much of the catalyst research for petroleum refining observed and described during the WTEC panel's visits focused on sulfur removal. The method used to remove sulfur depends on whether sulfur is present as hydrogen sulfide (H_2S) or organosulfur compounds. Two methods have been developed to remove H_2S; adsorption and absorption. Zinc oxide (ZnO) is most frequently used to adsorb H_2S (Othmer 1994; Armor 1999). Zinc oxide reacts with H_2S at 340–390°C to form zinc sulfide, ZnS (Armor 1999). Commonly used absorbents are aqueous solutions of organic amines such as monoethanol amine, diethanol amine, and triethanol amine.[4]

The removal of organosulfur compounds via catalytic hydrodesulfurization (HDS) is typically carried out using aluminum oxide (Al_2O_3) -supported cobalt-molybdenum (Co-Mo)- or nickel-molybdenum (Ni-Mo) -based catalysts. This reaction converts organosulfur compounds into H_2S, which can be subsequently removed. Although the operating temperature for hydrodesulfurization generally ranges from 300–400°C, the operating pressure and the space velocity depend on the nature of the sulfur compounds to be removed. The severity of conditions typically increases in the following order: mercaptan<benzothiophene<alkyl benzothiophene<dibenzothiophene<alkyl dibenzothiophene. Organosulfur compounds in natural gas can be removed using low pressures; however, significantly higher pressures (20–40 atm) are typically required to desulfurize liquid fuels including naphtha. Deep hydrodesulfurization typically involves pressures in the range of 60 to 100 atm and relatively low liquid hourly space velocities (LHSV) of 0.75 to 1.0 hr^{-1} to remove

[4] For additional information about hydrodesulfurization and other hydrotreating reactions, the reader is directed to books by Topsøe and Carnell (e.g., Topsøe, Clausen, and Massoth 1996; Carnell 1989).

the most refractory sulfur compounds (e.g., 4- or 6-methyl dibenzothiophene and 4,6-dimethyl dibenzothiophene). Improved materials and processes are being sought to reduce the consumption of hydrogen and improve product selectivities.

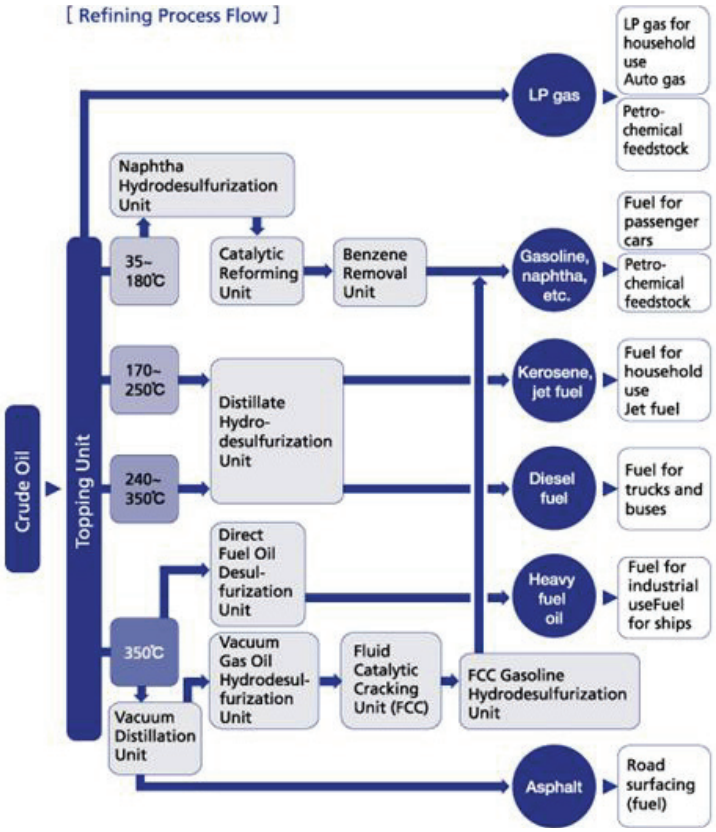

Figure 6.3. Image of refinery unit and process flow diagram for the conversion of crude oil into low-sulfur commercial liquid and gas products (http:// www.cosmo-oil.co.jp/eng/oilbusiness/refining.html).

As with most catalysts, performance is determined by the composition and structure, which are in turn determined by the preparation methods. Conventional methods for the preparation of hydrotreating catalysts initially proceed through oxide precursors supported on high-surface-area carriers (Figure 6.4). These oxide domains are sulfided to produce catalytic species that typically are nonuniform in terms of chemistry and morphology.

Institut Français du Pétrole

Researchers at the Institut Français du Pétrole (IFP) (see site report, Appendix D) are investigating novel precursors, supports, and methods for the preparation of catalysts with greater uniformity and better performance. One strategy involves the use of well-defined precursors in which most or all of the key chemistries and structures are incorporated. Karin Marchand and coworkers are using three types of precursors for the preparation of well-defined catalysts: (1) inorganic polyoxometallates and heteropolyanions (Cabello, Botto, and Thomas 2002; Martin et al 2004; Bergwerff et al. 2005), (2) inorganic cationic sulfides (Martin et al. 2005), and (3) MoS_x nanoparticles (Costa et al. 2007; Marchand et al. 2002). They report that neutral and cationic cubane-type complexes are particularly effective, yielding uniform, highly dispersed domains on supports including Al_2O_3 and zeolites (Figure 6.5) and catalysts with high intrinsic activities and good selectivities to C-S bond activation over C=C bond hydrogenation. This is an important finding because the interaction of most organometallic clusters with oxide supports causes decomposition and rearrangement of the elements (Choplin et al. 1993; Brenner and Thompson 1994; Gates 1995, 2000; Chotisuwan et al. 2007).

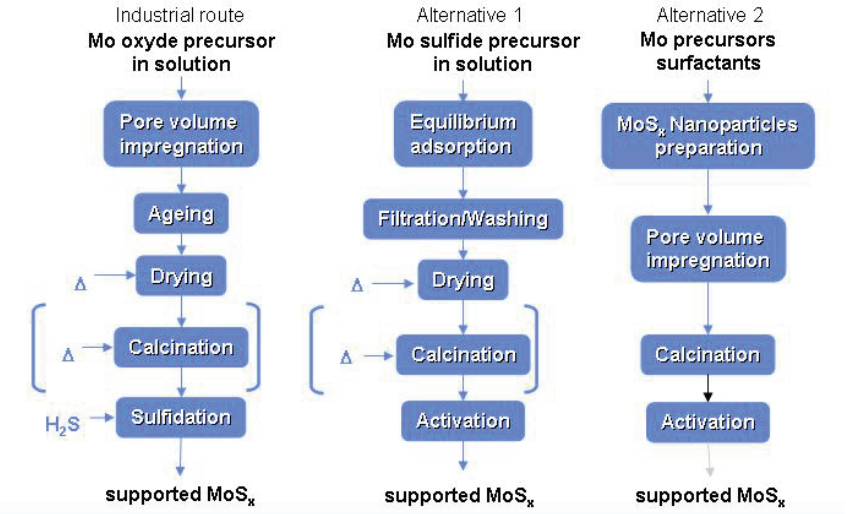

Figure 6.4. Effects of precursor and preparation conditions on structure and function of hydrotreating catalysts: l*eft*: typical; *center and right*: 2 alternatives being studied by IFP (courtesy of K. Marchand, IFP).

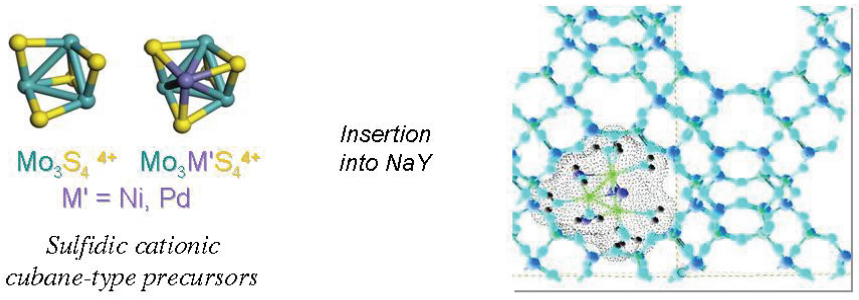

Figure 6.5. Mixed M-Mo cubane-type precursors (M is typically Ni, Pd, and Co) have been reported to yield smaller particles and better interactions between Mo and the promoter than those for conventionally prepared catalysts (courtesy of K. Marchand, IFP).

The IFP researchers also reported that relatively narrow particle sizes were achieved for MoS_x nanoparticles synthesized using a reverse microemulsion technique, although inhibition of HDS by residue from the surfactants could be a challenge. Raybaud and coworkers are using density functional theory (DFT) to model key interactions of the metal and metal sulfide moieties with oxide supports, including Al_2O_3 and TiO_2, with a focus on defining the density of active sites (Digne et al. 2002 and 2004; Arrouvel, Digne, et al. 2004; Dzwigaj et al. 2005; Arrouvel, Toulhoat, et al. 2004; Raybaud 2007; Arrouvel et al. 2006). A particularly interesting observation was that MoS_2 can grow "epitaxially" on TiO_2, thus producing a high degree of M-edge sites (Figure 6.6) that are believed to be hosts for the catalytically active sites for HDS (Schweiger et al. 2002).

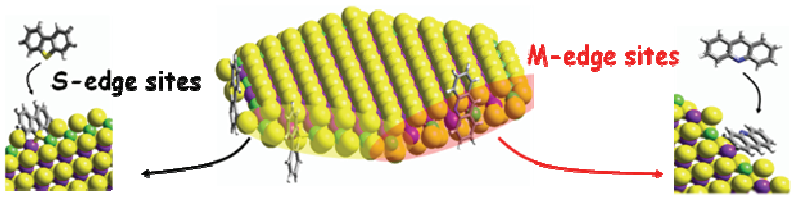

Figure 6.6. Schematic of Mo sulfide domain on oxide support with coordination of organosulfur and aromatic species (Raybaud 2007, 76).

Consiglio Nazionale delle Ricerche (Italy)

Francesca Deganello and coworkers at the Consiglio Nazionale delle Ricerche (CNR) Institute of Nanostructured Materials (INSM) in Palermo, Italy (see CNR site report, Appendix D) are investigating the use of mesoporous oxides including hexagonal mesoporous silica (HMS) as "active" supports for cobalt, gold, and lead. As illustrated in Figure 6.7, the resulting catalysts are active and selective for thiophene HDS, and a bifunctional mechanism was proposed with Brønsted acid sites serving to activate the organosulfur compound for protonation on the metal domains (Venezia et al. 2007a, 2007b; Liotta et al. 2007a, 2007b). This theme of deconvoluting the reaction pathways and producing domains to catalyze the key intermediate steps provided guidance for the design of catalysts for HDS and other reactions.

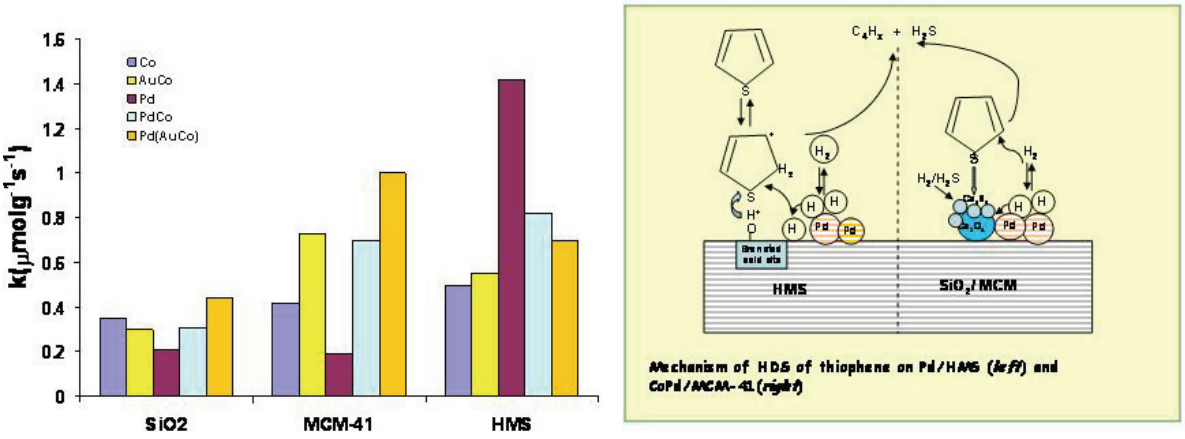

Figure 6.7. Mesoporous silica-supported Co, Au, and/or Pd catalysts for thiophene HDS. The superior activity, in particular for the Pd/HMS catalyst, is explained based on a bifunctional mechanism involving acid sites on the support (CNR/ISMN; courtesy of R. Psaro).

Catalysts for Syngas Conversion

Globally there is increased pressure to reduce fossil fuel imports and develop technologies to convert indigenous resources into liquid fuels that can be used and transported conveniently. With 13% of the world's proven reserves, China has enough coal to sustain its economic growth for a century or more, and it is investing in the development of technologies to convert coal into liquid transportation fuels. An attractive strategy involves the oxidation of coal into mixtures of CO and H_2 (syngas), then using a Fischer-Tropsch synthesis (FTS) process, converting this syngas into liquid fuels. The FTS reaction produces hydrocarbons and oxygenates from syngas that can be derived from any carbonaceous material, including biomass and coal (Bartholomew 1990; DOE 2008; equation 6.1).

$$CO + 2H_2 \rightarrow -CH_2- + H_2O \qquad \Delta H^\circ = -165 \text{ kJ/mol} \qquad (6.1)$$

This process has several advantages over the biochemical processes that are being developed for biomass conversion. The FTS hydrocarbons and oxygenates typically have higher energy densities than ethanol and biodiesel and can be blended with or substituted directly for conventional liquid transportation fuels such as diesel and gasoline. In addition, syngas can be produced from a wide range of carbonaceous materials, including the cellulose-rich portion of biomass (e.g., stover) that is difficult to convert using biochemical processes. Relative to conventional diesel, synthetic liquid fuels from FTS produce significantly lower NO_x, particulate, hydrocarbon, and CO emissions (Kochloefl 1997). The water gas shift (WGS) reaction is typically used to increase the H_2/CO ratios for syngas to levels suitable for FTS, and the FTS is carried out at 180–250°C and pressures ranging from 20–40 bar using Co-, Fe-, and Ni-based catalysts. Improvements in selectivity and activity are being sought through refinements in the catalyst structure and composition.

University of Utrecht (The Netherlands)

Krijn de Jong from Utrecht University (see site report, Appendix D) described to the WTEC panel work to determine the effect of particle size on FTS activity. In one example, the FTS activity for a Co/C catalyst was illustrated to go through a maximum for Co particles that were ~6 nm (Bezemer 2006; Figure 6.8). The chemistry and structure of these catalysts were characterized using chemisorption, X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM).

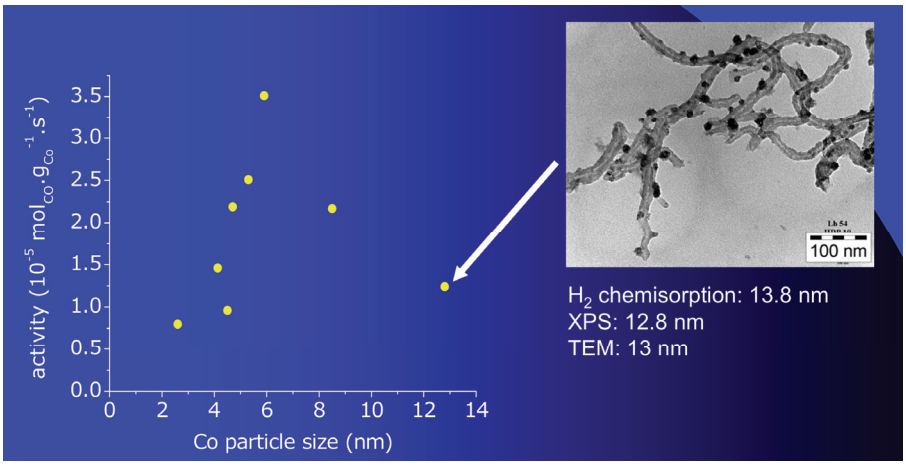

Figure 6.8. Effect of particle size on Fischer-Tropsch synthesis activities of carbon-nanofiber-supported Co catalysts. Measurements were carried out at 220°C, 1 bar, and a H_2/CO ratio of 2 (Bezemer 2006).

This group also investigated the effects of different calcination gases and conditions on the morphological and functional properties of oxide-supported Co catalysts. For example, they have reported that Co/SiO_2 catalysts calcined in NO possessed much smaller Co particles than catalysts calcined at the same temperature in air (Figure 6.9). As expected, reaction rates for the NO-calcined materials were higher than those for the air-calcined materials.

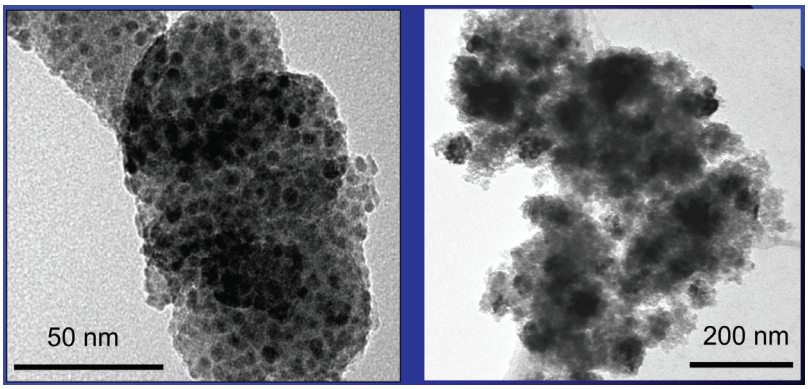

Figure 6.9. Transmission electron micrographs of Co/SiO_2 catalysts following calcination in (a) NO and (b) air, then reduction at 550°C. Particle sizes were significantly smaller for the NO-calcined catalyst, and the Fischer-Tropsch synthesis reaction rates were higher (courtesy of K. De Jong).

Institute of Coal Chemistry/Chinese Academy of Sciences (China)

Researchers at the Institute of Coal Chemistry of the Chinese Academy of Sciences (ICC/CAS; see site report, Appendix C) are developing nanostructured catalysts for the FTS and CH_4 (methane) dry reforming reactions using methods ranging from quantum chemistry and molecular dynamics to reactor simulation. The

efforts have yielded new combinations of catalysts, including Fe carbides in MoS_2, and a potentially new nanophase MoS_2 was described by Yuhan Sun and coworkers (Li et al. 2004, Li et al. 2007). The performance of a variety of catalysts is being evaluated in major pilot plant facilities. Figure 6.10 illustrates pilot plants for coal gasification and FTS. These units have the capacity to convert 100 tons of coal per day into syngas and then Fischer-Tropsch liquids. Work at this scale is typically not found in academic or government laboratories in other countries; however, investments of this scale are increasing in China.

Figure 6.10. (*Left*) ICC/CAS can process 100 tons/day long rank coal in a fluidized bed gasification pilot/demonstration plant; a higher-pressure process is under development for higher capacity. (*Right*) shows a large Fischer-Tropsch slurry demonstration unit (Fe catalysts).

PRODUCTION OF HYDROGEN

More than 50 million tons of hydrogen are produced globally each year. Nearly half of this hydrogen is derived from natural gas, 30% from petroleum, ~18% by reducing water with coal, and ~2% from water via electrolysis. The conversion of fossil resources into hydrogen typically involves a desulfurizer to remove sulfur compounds from the feed, reformer to produce syngas, and a CO-cleanup step to reduce the amount of CO (Figure 6.11). Carbon monoxide that is in reformer effluent can severely and irreversibly poison downstream catalysts, including those used in ammonia synthesis and proton exchange membrane fuel cells (PEMFC); therefore CO must be reduced to ppm levels (Carrette, Friedrich, and Stimming 2000; Parsons and Vandernoot 1988; Capon and Parsons 1973). This is accomplished via the water gas shift (equation 6.4), followed by CO preferential oxidation or methanation.

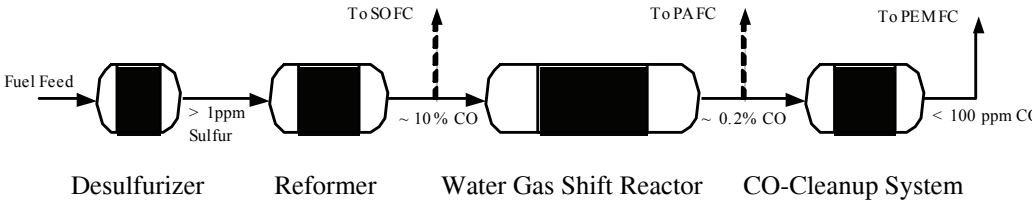

Figure 6.11. Schematic of key steps in the conversion of fossil resources into hydrogen for fuel cell applications.

The syngas is most often produced using steam reforming and/or partial oxidation reactions. Key reactions in the steam reformer are listed below.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^\circ = 206 \text{ kJ/mol} \qquad (6.2)$$

$$C_nH_{2n+2} + mH_2O \rightarrow nCO + (m+n+1)\,H_2 \qquad (6.3)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^\circ = -41 \text{ kJ/mol} \qquad (6.4)$$

The reforming of higher hydrocarbons typically starts with decomposition into lower-molecular-weight species that can more efficiently react with steam. Oxide-supported Fe, Co, and Ru catalysts are effective for the FTS reaction, although they can suffer from deactivation by coke deposition. This coke is produced through polymerization of the various reactive olefinic species on the surface. The partial oxidation reactions are exothermic and can be carried out without (noncatalytic partial oxidation) or with a catalyst (catalytic partial oxidation). The main advantage of the noncatalytic partial oxidation process is that it can be used to process almost any hydrocarbon feedstock from natural gas to petroleum residue (equations 6.5 and 6.6).

$$CH_4 + 0.5\ O_2 \rightarrow CO + 2H_2 \qquad \Delta H^\circ = -\ 36\ kJ/mol \qquad (6.5)$$

$$2C_nH_{2n+2} + nO_2 \rightarrow 2nCO + 2(n+1)H_2 \qquad (6.6)$$

Other reactions like total combustion and steam reforming also take place to some extent during the partial oxidation process (Pena, Gomez, and Fierro 1996). Typically, noncatalytic partial oxidation reactions are carried out at very high temperatures and employ smaller reactors than those used for steam reforming reactions. Autothermal reforming combines partial oxidation and steam reforming to create a near thermally neutral process. The partial or total oxidation of the fuel is carried out in the front end of the reactor and is followed by steam reforming. The heat generated via partial oxidation provides the heat required for the endothermic steam reforming reactions. Suitable feedstocks for autothermal reforming are CH_4-rich natural gas, CH_3OH and heavier hydrocarbons, up through naphtha (Gunardson 1998).

The water gas shift reactor typically constitutes a third of the size and cost of the systems used to convert fossil resources into hydrogen. As such, it is not surprising that much of the research in the area of hydrogen production focuses on the development of better-performing WGS catalysts. The WGS reaction is commercially carried out in two stages with a high-temperature-shift (HTS) stage employing Fe-Cr-based catalysts and a low-temperature-shift (LTS) stage using Cu-Zn-Al-based formulations. While the Fe-Cr HTS catalysts are robust and to some extent sulfur-tolerant, their activities are low. Furthermore, some countries prohibit the use of these Fe-Cr-based catalysts because of the potential for producing genotoxic hexavalent Cr (EPA 1998). The Cu-Zn-Al LTS catalysts are highly active but very susceptible to deactivation

University of Udine, Consiglio Nazionale delle Ricerche (Italy)

Researchers at the University of Udine, in connection with the CNR (see CNR site report, Appendix D), are manipulating characteristics of the metal particles and supports to enhance the overall reaction rate for WGS. Alessandro Trovarelli and coworkers described tailor-made rare earth oxide- and ZrO_2-supported Au and Pt catalysts with high activities (Tibiletti et al. 2006). They also reported that the {100} surface of CeO_2, a support that is used in several high-activity WGS catalyst formulations, is more active for the reduction of water than the other facets (Aneggi et al. 2005). Methods are being developed to increase the exposure of {100} facets for CeO_2-supported catalysts. Figure 6.12 shows high-resolution transmission electron micrographs illustrating CeO_2 supports with high preferential exposures {100} planes.

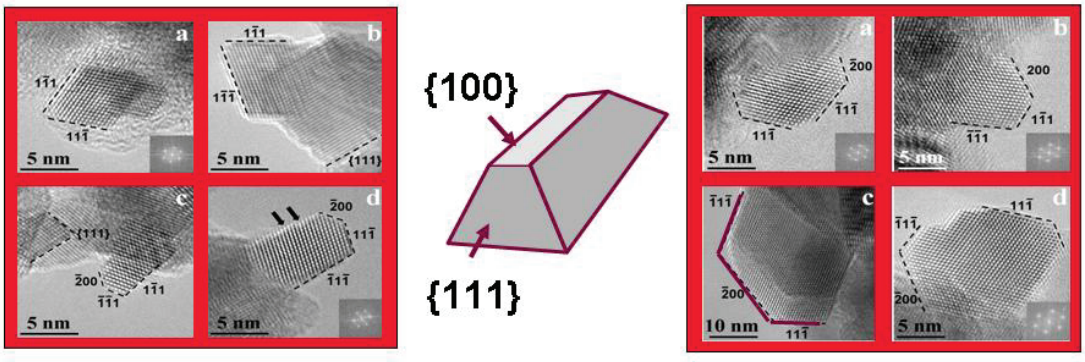

Figure 6.12. CNR/University of Udine researchers are developing novel water gas shift catalysts via support optimization. For CeO_2 supported catalysts, supports are modified to enhance CO oxidation, preferentially exposing the more active {100} surface.

University of Trieste, Consiglio Nazionale delle Ricerche (Italy)

Researchers at Italy's University of Trieste, in connection with CNR (see CNR site report, Appendix D), are working on preferential oxidation (PrOx) and WGS catalysts for the purification of hydrogen-rich reformate, the design of nanostructured photocatalysts, and development of mixed-oxide cathodes for solid oxide fuel cells. Mauro Graziani and coworkers described methods to encapsulate preformed metal nanoparticles in oxides as a strategy to enhance catalyst durability (Montini, De Rogatis, et al. 2007; Montini, Condó, et al. 2007; Figure 6.13). Active species, including Rh, Ni, and Cu, have been encapsulated in porous Al_2O_3 and CeO_2-ZrO_2-Al_2O_3. They argued that this architecture inhibits sintering of the active species but allows reactants and products to diffuse through pores in the oxide. Enhanced durability was demonstrated for several WGS and preferential oxidation catalysts, including Au/CeO_2.

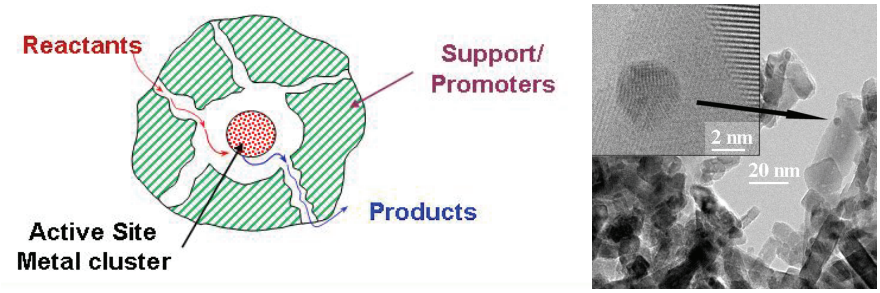

Figure 6.13. To enhance the stability of PrOx and WGS catalysts, methods have been developed at CNR/University of Trieste to encapsulate preformed metal nanoparticles in porous oxides. This architecture (*left*) allows the reactants and products access to the catalytically active metal while inhibiting sintering. At *right* is a high-resolution transmission electron micrograph illustrating an encapsulated metal particle.

Instituto di Chimica dei Composti OrganoMetallici (Italy)

Claudio Bianchini and coworkers from the Instituto di Chimica dei Composti OrganoMetallici (University of Florence and CNR) (see CNR site report, Appendix D) are investigating catalytic systems for the production of hydrogen, including Fe-Ni-Co/Al_2O_3 ethanol steam reforming catalysts, and electrocatalysts for the electrolysis of H_2O, NH_3, and renewable feedstocks such as glycerol. They are also detailing the reaction pathways for these systems. For example, they propose that the conversion of glycerol proceeds through several value-added intermediates, including glyceric acid, tartronic acid, glycolic acid, and oxalic acid, to form formic acid and CO_2 as products.

Tokyo Metropolitan University Department of Applied Chemistry

Haruta and coworkers at Tokyo Metropolitan University (TMU) Department of Applied Chemistry (see site report, Appendix C) have done pioneering work in the area of nanostructured Au catalysts and continue to develop these materials for a variety of applications, including WGS (Haruta et al. 1987; Tsubota et al. 1991; Sakurai, Tsubota, and Haruta 1993; Haruta et al. 1993; Haruta and Date 2001; Haruta 2002; Ishida and Haruta 2007). Their work has yielded catalysts with nanoscale Au particles (Figure 6.14) that are more active than most other materials, including Cu-Zn-Al and supported Pt catalysts. They report 100% conversion to CO_2 with no CH_4 production at high space velocities and temperatures up to 623 K. Stability issues, however, remain to be addressed, because these materials tended to deactivate over time, in particular when exposed to high levels of moisture (Kolmakov and Goodman 2001; Costello et al. 2003; Kim and Thompson 2005; Goguet et al. 2007; Karpenko et al. 2007).

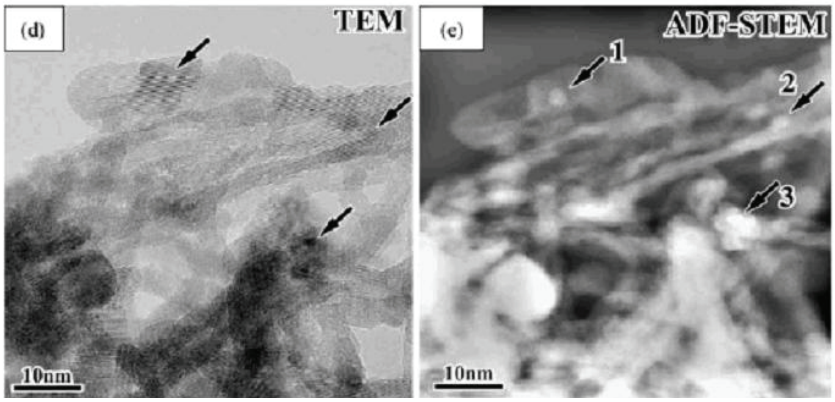

Figure 6.14. High-resolution transmission electron micrographs of highly active Au/CeO_2 WGS catalysts. These materials achieved 100% conversion to CO_2 with no production of methane for temperatures up to 623 K.

Tsinghua University (China)

Research at Tsinghua University (see site report, Appendix C) is investigating ways to control the structure of catalysts. Boqing Xu and coworkers describe the use of electrochemical methods to produce nanostructured materials. High dispersions of metals including Ni, Au, and Pt have been achieved for a variety of support materials including ZrO_2 and TiO_2 (Wang, Wu, and Xu 2005; Wu, Chen, and Xu 2005; Li, Wu, and Xu 2006; Wu et al. 2007; Yu and Xu 2006 and 2007; Wu, Liu, and Xu 2007; Xin, Wang, and Xu 2005; Xin, Hui, and Xu 2005; Zhang, Shi, and Xu 2007). The resulting catalysts were active for the dry reforming, CO oxidation, diene hydrogenation, and hydrogen electrocatalytic oxidation reactions.

Tianjin University (China)

Changjun Liu from Tianjin University (China) (see site report, Appendix C) described the use of plasma treatment methods to alter the structure and function of catalytic materials. This low-temperature treatment yielded structures that are very different from those for catalysts produced using more conventional methods. In one example, they observed that the orientation of Pt particles on TiO_2 subject to plasma treatment was different from the orientation of those produced using thermal treatment (Figure 6.15). The plasma treatment process was also used to produce Ni/Al_2O_3 CH_4 dry reforming catalysts with higher activities and reduced susceptibility to coking.

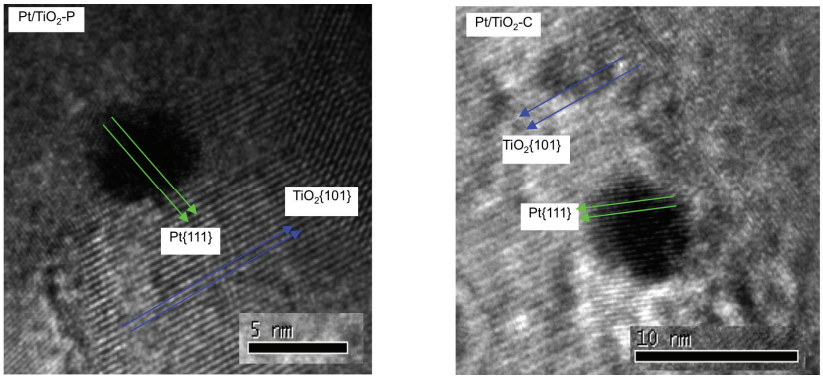

Figure 6.15. High-resolution transmission electron micrographs comparing the orientations of Pt particles relative to the TiO_2 supports for catalysts treated using (*left*) conventional high-temperature thermal treatments and (*right*) low-temperature, plasma-based treatments.

FUEL CELL RESEARCH

Key challenges for fuel cells include their high cost and poor durability. There is substantial research on electrocatalysts for fuel cells in both Asia and Europe; however, the WTEC panel was only able to visit a few laboratories doing fuel cell research. Several types of fuel cell are being investigated, including polymer electrolyte membrane fuel cells (PEMFC), solid oxide fuel cells (SOFC), as well as molten carbonate, direct methanol, and direct carbon fuel cells. Much of the work can be characterized as applied research and development.

University of Trieste, Consiglio Nazionale delle Ricerche (Italy)

Graziani and coworkers from University of Trieste (see CNR site report, Appendix D) are developing $LaNi_{0.6}Fe_{0.4}O_3$ and $La_{(1-y)}Sr_yNi_{0.6}Fe_{0.4}O_3$ cathodes for SOFCs. This material was reported to have much higher ionic conductivities than $LaNi_{0.6}Fe_{0.4}O_3$ (Bevilacqua et al. 2006). Experimental and theoretical studies are being used to optimize performance characteristics of these materials.

Tsinghua University (China)

Boqing Xu and coworkers from Tsinghua University (see site report, Appendix C) are developing methods to disperse Pt on Au cores for use in PEMFCs (Zhao, Wu, and Xu 2005; Zhao and Xu 2006). This architecture would allow greater utilization of the expensive Pt. These catalysts achieved near 100% Pt utilization due to the dispersion of Pt domains smaller than 1 nm. The synthetic process can also be used to create core-shell geometries with Pt shells on Au cores.

Tianjin University (China)

Yongdan Li from Tianjin University (see site report, Appendix C) described a relatively novel type of fuel cell, the direct carbon fuel cell (DCFC). Carbon is electrochemically oxidized using graphite electrodes and molten carbonate electrolytes according to the following reactions (equations 6.7 and 6.8):

$$C + 4OH^- \rightarrow CO_2 + 2H_2O + 4e^- \quad (6.7)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4\ OH^- \quad (6.8)$$

Efficiencies near 40% can be achieved with this type of device. A hybrid concept was described with a reactor to decompose CH_4 to carbon, a DCFC to oxidize the carbon, a PEMFC to convert the H_2, and a waste heat recovery system (Cao et al. 2004; Chen et al. 2004; Qian, Liu, et al. 2003; Qian, Wei, et al. 2003; He et al. 2006; Chen et al. 2003). Overall efficiencies near 100% were suggested. These systems could be used as an alternative to coal-fired power plants.

In addition to efforts to develop more durable and lower-cost catalysts, research at the *Dalian Institute of Chemical Physics* (see site report, Appendix C) and *Shanghai Jiao Tong University* focuses on large-scale, multistack demonstrations. The associated laboratories are large and fairly well equipped.

ENVIRONMENTAL CATALYSIS

Environmental catalysis remains an important area with regard to the conversion of fossil fuels. With the increasing number of vehicles, in particular in developing countries, the need for more effective emission control catalysts is growing. There is also growing interest in the development of processes to recycle CO_2 into useful products. Nearly 30 billion tons of CO_2 are emitted into the environment annually due to human activity, including transportation and electricity production. With growing evidence linking this CO_2 to disruptive global climate change and predictions that CO_2 emissions will double in the next 50 years, the remediation of CO_2 has attracted considerable attention. In a recent report from the National Academies, managing atmospheric CO_2 is listed as one of 14 Grand Challenges for the 21st Century—along with major scientific and engineering challenges like the discovery of better medicines, securing cyberspace, and providing access to clean water (National Academy of Engineering 2008). Technologies are being developed to capture and sequester CO_2; however, there are concerns about the capacities and the long-term

environmental impacts of storing CO_2 in, for example, geologic formations. Of course, biological processes including photosynthesis provide highly selective routes for CO_2 and H_2O conversion into carbohydrates, but the rates are too low for large-scale conversion of anthropogenic CO_2. Consequently, these are opportunities for the discovery and development of new catalysts.

Three-Way Catalysis

Toyota Motor Corporation, Higashi-Fuji Technical Center

Researchers at the Toyota Motor Corporation's Higashi-Fuji Technical Center (see site report, Appendix C) are working to deconvolute the complex chemistry and behavior of three-way catalysts, in terms of both reactivity and deactivation. Results from high-resolution transmission electron microscopy, X-ray absorption spectroscopy, and X-ray photoelectron spectroscopy indicate that Pt on Al_2O_3-ceria-zirconia-yttria (CZY) support produces two different types of sites. Platinum that resides on the Al_2O_3 is weakly bound and agglomerates into zero-valent particles; platinum on the CZY is more strongly bound, maintains a high degree of dispersion, and is oxidized. Figure 6.16 illustrates the presence of relatively large Pt particles on Al_2O_3 portions of the catalyst and highly dispersed domains on the CZY portion of the catalyst.

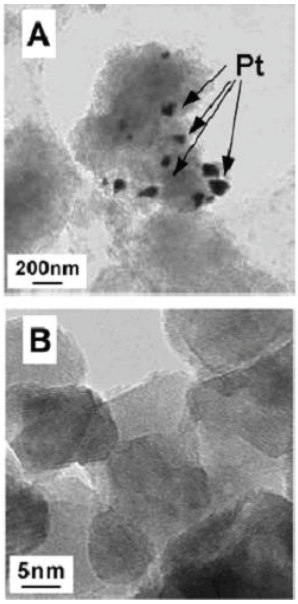

Figure 6.16. Transmission electron micrographs illustrating the degree of Pt sintering on (A) Al_2O_3 and (B) CZY after treatment at 800°C in air (Nagai et al. 2006).

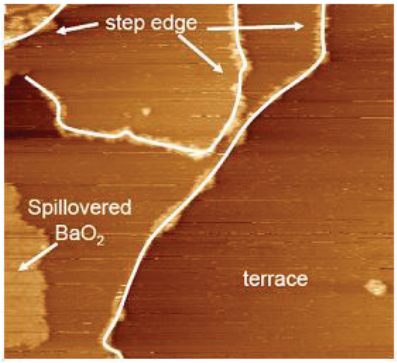

Figure 6.17. Scanning tunneling microscopy images of the oxidized Ba/Pt{111} surfaces with BaO_2 on the terraces.

NO_x Selective Catalytic Reduction

Toyota Motor Corporation, Higashi-Fuji Technical Center

Researchers at Toyota Motor Corporation's Higashi-Fuji Technical Center are also working on NO_x storage materials, most often incorporating barium. A variety of tools are being used in this research to provide insights regarding sites where oxygen interacts with barium, the mechanism for oxygen migration to platinum sites, changes in the chemistry of the platinum site, and ultimately, mechanisms for the production of nitrates on the surface. Of particular importance is work in collaboration with Michael Bowker at Cardiff University (UK) (see site report, Appendix D) using scanning tunneling microscopy (STM). The results suggest that NO_x storage proceeds via dissociation of O_2 on the Pt step edges, then reaction of atomic oxygen with barium on the terraces to produce BaO and BaO_2. Subsequently, NO and O_2 react with BaO_2 on the terrace to form O-Ba-NO_2 species. The adsorbed NO_2 can diffuse back to the step edge, where it reacts with

additional oxygen and BaO to form $Ba(NO_3)$. The adsorbed NO_2 is believed to be the critical intermediate during NO_x reduction. Figure 6.17 (above) is an STM image illustrating the Pt{111} surface with BaO_2 on the terraces and NO_2 species at the step edges.

Consiglio Nazionale delle Ricerche (Italy)

Deganello and coworkers from the CNR/INSM (Palermo) are using sol-gel methods to enhance the thermal stabilities of Pt-Pd/CeO_2-ZrO_2 catalysts and thereby extend the window for lean NO_x reduction. In addition, they are developing Au/Al_2O_3-CeO_2-based NO_x reduction catalysts with enhanced thermal stabilities and higher N_2 selectivities.

Pio Forzatti from the *Politecnico di Milano* (see site report, Appendix D) described research to better understand mechanisms for NO_x selective catalytic reduction (SCR) with NH_3.

CO_2 Reduction

While a number of reactions of CO_2 are thermodynamically possible, many are kinetically hindered, therefore, catalytic conversion of CO_2 typically requires an energy-intensive, high-temperature process (~1000 K) and the use of hydrogen as a reductant.

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta G° = -9.1 \text{ kJ/mol} \qquad (6.9)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \Delta G° = -130.7 \text{ kJ/mol} \qquad (6.10)$$

$$CO_2 + 3H_2 \leftrightarrow \tfrac{1}{2} C_2H_5OH + 3/2\ H_2O \qquad \Delta G° = -48.7 \text{ kJ/mol} \qquad (6.11)$$

$$CO_2 + 7/2H_2 \leftrightarrow \tfrac{1}{2} C_2H_6 + 2\ H_2O \qquad \Delta G° = -96.4 \text{ kJ/mol} \qquad (6.12)$$

$$CO_2 + CH_4 \leftrightarrow 2CO + 2H_2 \qquad \Delta G° = 170.4 \text{ kJ/mol} \qquad (6.13)$$

The Sabatier reaction (equation 6.10) is among the most thermodynamically favorable processes; it has been investigated by the U.S. National Aeronautics and Space Administration (NASA) as a means of converting CO_2 into hydrocarbon fuels for long interplanetary trips. Transition metals including Ru, Ni, and Fe dispersed on supports like Al_2O_3 catalyze this reaction but have relatively low activity and require temperatures in excess of 400°C. These high temperatures diminish the overall efficiency of the process. The dry reforming of CO_2 with CH_4 (equation 6.13) has been extensively investigated in a number of countries, with the goal of developing catalysts that give high yields of syngas without significant deactivation due to coking. A variety of types of supported metal catalysts have been explored, including Ni and noble metal catalysts.

Electrochemical processes offer an attractive strategy for the reduction of CO_2 especially when driven by electricity produced directly or indirectly from solar energy or other carbon-neutral sources (e.g., nuclear energy). Electrochemical potentials for the reduction of CO_2 to C_1 chemicals are listed in Table 6.1. A number of metals and semiconductors are capable of catalyzing these types of reactions. For example, electrodes containing metal phthalocyanines have been reported to reduce CO_2 to formic acid; however, the rates were low (Meshitsuka, Ichikawa, and Tamaru 1974). Iron, Co, and Ni macrocyclic compounds, including polypyrrole/Schiff-base complexes of Ni, are also capable of reducing CO_2, typically to formate (Dhanasekaran et al. 1999; Ogata et al. 1995; Beley et al. 1986). The reduction of CO_2 to CH_4, C_2H_4 and alcohols has been demonstrated at fairly high yields using metallic copper electrodes and aqueous electrolytes (Hoshi and Hori 2003); however, the catalytic activities were low and the electrodes quickly deactivated.

Table 6.1. Potentials for Electrochemical Reduction of CO_2

Reaction	$E° (V_{SHE})$
$CO_2(g) + 2H^+(aq) + 2e- \rightarrow HCOOH(aq)$	-0.11
$CO_2(g) + 2H^+(aq) + 2e- \rightarrow CO(g) + H_2O(l)$	-0.10
$CO_2(g) + 4H^+(aq) + 4e- \rightarrow CH_2O(aq) + H_2O(l)$	-0.028
$CO_2(g) + 6H^+(aq) + 6e- \rightarrow CH_3OH(aq) + H_2O(l)$	+0.031
$CO_2(g) + 8H^+(aq) + 8e- \rightarrow CH_4(g) + 2H_2O(l)$	+0.17

University of Messina (UNIME; Italy)

Gabriele Centi and coworkers at the University of Messina (see site report, Appendix D) have demonstrated several electrocatalysts including Cu-based materials for the reduction of CO_2 into long chain hydrocarbons and alcohols using an electrochemical cell that resembles a proton exchange membrane fuel cell (Centi et al. 2007; Perathoner et al. 2007). The cells are operated at ambient conditions. As shown in Figure 6.18, a variety of products were formed, including large amounts of aromatic and C8-C9 hydrocarbons. Efficiencies near 30% were reported for this particular process.

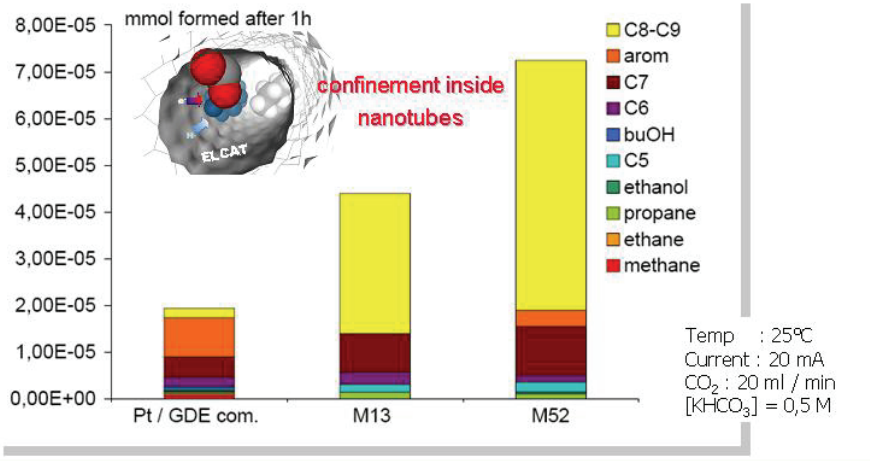

Figure 6.18. Electrocatalytic conversion of CO_2 into hydrocarbons and alcohols with efficiencies near 30% at ambient conditions have been reported by Centi and coworkers. This figure illustrates production rates for several electrocatalysts including metals confined in nanotubes (courtesy of G. Centi).

University of Tsukuba (Japan)

Researchers at the University of Tsukuba (see site report, Appendix C) are developing bifunctional oxides for the reduction of CO_2 with alcohols and diols to produce organic carbonates (Figure 6.19). The bifunctional oxides possess acid and base sites to facilitate insertion of CO_2 into the O-H bond of the alcohol.

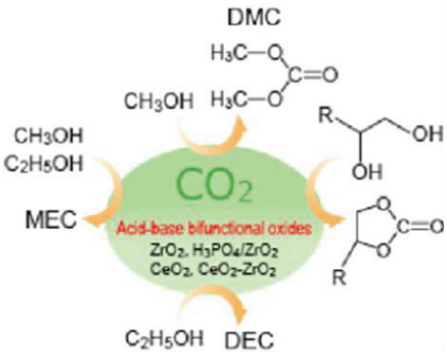

Figure 6.19. The University of Tsukuba is exploring strategies for reduction of CO_2 with alcohols over acid-base bifunctional oxides. Products including organic carbonates can be formed.

Institute of Coal Chemistry of the Chinese Academy of Sciences

Researchers at the Institute of Coal Chemistry of the Chinese Academy of Sciences are investigating the use of a variety of reductants including NH_3 to produce a variety of chemicals.

SUMMARY

Given that global energy needs will continue to be satisfied primarily using fossil resources for the foreseeable future, the importance of catalysis for the production of liquid transportation fuels and hydrogen and for emissions control cannot be overstated. New challenges including those associated with carbon dioxide (CO_2) management also present important opportunities. The WTEC panelists were privileged to witness a great breadth and depth of important energy-related catalysis research in both Europe and Asia. Other observations of the panel are summarized below.

Project Highlights: Energy-Centered Catalysis R&D

European Union

- Modeling of the interactions of MoS_2 and oxide supports for HDS catalysts (Raybaud and coworkers, Institut Français du Pétrole, France)
- Correlations of Co particle size and FTS activity, and use of NO as calcining agent (de Jong and coworkers, University of Utrecht, Debye Institute, The Netherlands)
- Identification of the influence of CeO_2 faceting on WGS activity (Trovarelli and coworkers, University of Udine/CNR, Italy)
- Descriptions of Ba oxide morphologies on Pt NO_x storage materials (Bowker and coworkers, Cardiff University, UK)
- Electrocatalytic reduction of CO_2 to hydrocarbons (Centi and coworkers, University of Messina, Italy)

Asia

- Continued development of nanostructured Au catalysts (Haruta and coworkers, Tokyo Metropolitan University Department of Applied Chemistry, Japan)
- Use of electrochemical methods (Xu and coworkers, Tsinghua University, China) and plasma methods (Liu and coworkers, Tianjin University, China) to produce nanostructured catalysts
- Development of DCFC as an alternative to coal combustion (Li and coworkers, Tianjin University, China)

Regional Characteristics of Catalysis R&D for Improving Fossil Energy Production

European Union

- Research is highly integrated both nationally and across the European Union
- Academic research is viewed as the driver for innovation and depended upon by industry; thus, there is work on fundamental as well as applied issues
- There are substantial investments in hydrotreating, catalytic cracking, and environmental catalysis

Asia

- Research in China is addressing immediate national issues and consequently tends to be highly applied; in some cases it might be better characterized as development
- Applied work in China tends to be focused on utilization of indigenous resources (e.g., coal gasification and FTS), with growing activities in environmental catalysis; much more coal gasification and FTS research than in the United States
- There is emphasis in China on large-scale demonstrations; many of these operations are coordinated with more fundamental work
- Research in Japan and Korea appear to be of similar character and funding as research being carried out in the United States

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CHAPTER 7

APPLICATIONS: CHEMICALS FROM FOSSIL RESOURCES

Vadim V. Guliants

INTRODUCTION

Heterogeneous catalysts enable many chemical transformations of fossil resources into useful products (Thomas and Thomas 1997; Gates 1992). Catalysts are responsible for the production of over 60% of all chemicals and are used in some 90% of all chemical processes worldwide (Council for Chemical Research 1998; Bartholomew and Farrauto 2005). According to a 2001 discussion of the impact of catalysis on the U.S. economy, "one-third of material gross national product in the U.S. involves a catalytic process somewhere in the production chain" (Morbidelli, Gavrillidis, and Varma 2001). Catalyst manufacturing alone accounts for over $10 billion in sales worldwide in four major sectors: refining, chemicals, polymerization, and exhaust emission catalysts. However, the value derived from catalyst sales is greatly eclipsed by the total value of the products that are produced, i.e., chemical intermediates, polymers, pesticides, pharmaceuticals, and fuels. The global annual impact of catalysis is estimated to be $10 trillion (Council for Chemical Research 1998). As we look to the future, heterogeneous catalysis increasingly holds the key to “green chemistry” and the promise of eliminating or at least dramatically curbing pollution from chemical and refining processes (Bowker 1998). Heterogeneous catalysis is key to many proposed green chemical processes targeted to cut back harmful emissions (Anastas and Warner 1998). The goal of catalysis for green chemistry is to tailor atomically the structure of the active and selective site in order to convert reactants directly to products without generating by-products that typically end up as waste (van Santen and Neurock 2006).

The majority of industrial catalysts contain an active component in the form of nanoparticles <20 nm in size that are dispersed onto high-surface-area supports. The importance of nanoparticles and nanostructure to the performance of catalysts has stimulated wide efforts to develop methods for their synthesis and characterization, making this area of study an integral part of nanoscience (Bell 2003). This chapter provides recent examples from the literature and from the institutions visited by the WTEC panel of how catalysis performance (i.e., activity and selectivity) is affected by the local size, shape, structure, and composition of catalyst particles employed in four major classes of organic reactions that underlie conversion of fossil resources to chemicals. These four classes are alkylation, dehydrogenation, hydrogenation, and selective oxidation. The chapter also highlights future trends in catalysis by nanostructured materials that are expected to result in detailed understanding of the effects of particle composition, size, and structure on catalyst performance, which will support better green chemistry for the future. Ultimately, the goal of studies in catalysis by nanostructured materials is to develop an understanding of these complex systems to a point where it will be possible to successfully exploit nanoscale phenomena by design to create new heterogeneous catalysts and green catalytic processes.

ALKYLATION

The alkylation of aromatic compounds is widely used in the large-scale synthesis of petrochemicals, fine chemicals, and intermediates (Ertl, Knözinger, and Weitkamp 1997). This reaction consists of the

replacement of a hydrogen atom of an aromatic compound by an alkyl group derived from an alkylating agent. If the hydrogen being replaced is on the aromatic ring, the reaction is electrophilic substitution, which requires an acid catalyst. If the hydrogen being replaced is on the side chain of an aromatic molecule, then base catalysts or radical conditions are needed.

Acid catalysts used for alkylation of aromatic hydrocarbons are Brønsted acids containing acidic protons, e.g., acidic halides such as $AlCl_3$ and BF_3, acidic oxides, zeolites, protonic acids—especially sulfuric acid, hydrofluoric acid, phosphoric acid—and organic cation exchange resins. The acidic halides and protonic acids are being rapidly replaced for large-scale applications by solid alkylation catalysts, especially zeolites, because these are much more desirable for environmental reasons. They are noncorrosive and offer additional advantages for controlling selectivity via their shape-selective properties. This brief overview focuses on recent developments related to the synthesis and applications of novel solid catalysts in the alkylation of aromatic compounds in which the nanoscale pore environment of a solid catalyst is exploited to achieve superior activity and shape selectivity.

The periodic mesoporous organosilicas (PMOs) represent one of the recent breakthroughs in the field of materials chemistry of mesoporous nanostructured materials (e.g., Asefa et al. 1999). PMOs are synthesized from the bridged organosilane precursors, $(R'O)_3SiR(OR')_3$ and possess some unique properties that cannot be obtained by other approaches, such as uniformly distributed organic groups in the mesoporous framework with maximum loading of 100%. Unlike fully inorganic variants of ordered mesoporous frameworks, PMOs exhibit a periodic arrangement of the hydrophobic organic layers (e.g., ethylene and benzene) and hydrophilic silica layers within the pore walls (see Figure 7.1) (Yang et al. 2004; Xia, Wang, and Mokaya 2005; Yang et al. 2005). Incorporation of heteroatoms in these PMOs provides a new approach for the synthesis of bifunctional mesoporous materials with crystal-like pore wall structure and novel catalytic properties in epoxidation (Ti), ammoxidation (Ru), and alkylation (Al) reactions (e.g., Wahab and Ha 2005 and references therein).

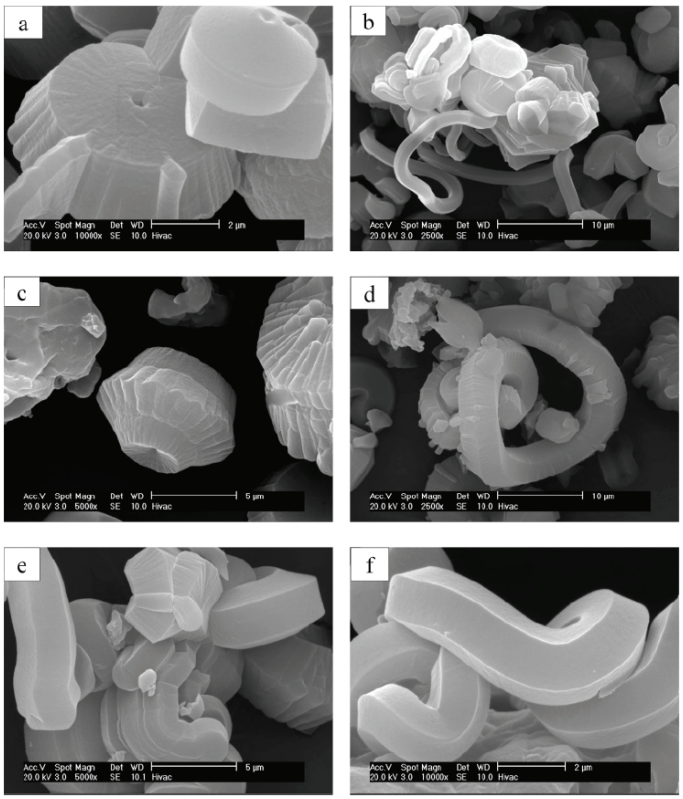

Figure 7.1. Representative SEM images of ethylene-containing hybrid mesoporous organosilica (Figure 3 from Xia, Wang, and Mokaya 2005).

In studies where tetrahedral Al species were incorporated into the PMO frameworks during synthesis of ethylene- (Yang et al. 2004; Xia, Wang, and Mokaya 2005) and benzene-bridged PMOs (Yang et al. 2005), the resultant PMO phases with both mesoscale (2.3–3.0 nm pore diameters, 4.6–5.1 nm d_{100}-spacings, and 2.1–2.6 nm thick walls) and molecular-scale periodicity possessed significantly improved hydrothermal stability, due to increased hydrophobic character and the incorporation of tetrahedral aluminum in the mesoporous framework. It was found that the ethylene-bridged mesoporous framework generated a greater amount of acid sites than the phenylene-bridged network with a similar Si/Al ratio and aluminum coordination environment. Consequently, the Al-containing ethylene-bridged PMO exhibited higher catalytic activity in alkylation of 2,4-di-*tert*-butylphenol with cinnamyl alcohol under identical reaction conditions (Yang et al. 2005). Moreover, periodic arrangement of organic layers in these materials offers a possibility to introduce several types of functional groups and even control their relative spacing on the mesopore surface, which together with metal substitution into their silica framework component may offer a new strategy for controlling multistep catalytic reactions in a single vessel.

Microporous zeolites have been widely used in industry as solid-acid catalysts for a variety of alkylation reactions. Significant mass transport limitations to and from the active sites located in micropores severely limit their performance (Davis 2002). To overcome these limitations, various strategies have been successfully pursued, such as the synthesis of nanosized zeolites (early work on colloidal zeolites Y and A by Schoeman et al. 1994), ultralarge-pore zeolites and zeolite analogs (VPI-5, JDF-20, UTD-1, CIT-5, SSZ-53, ECR-34, ITQ-21, etc.; see Corma 2003) and ordered mesoporous materials (MCM-41, SBA-15, FSM-16, etc.; see Wan and Zhao 2007). However, the use of these materials is rather limited, due to the difficulty of separating nanosized zeolite crystals from the reaction mixture, the complexity of the templates used for the synthesis of ultra large-pore zeolites, and the relatively low thermal and hydrothermal stability of ordered mesoporous materials. More recently, mesoporous zeolites from nanosized carbon templates have also been reported (e.g., Jacobsen et al. 2000), but their industrial applications are still limited by the complexity of the synthetic procedure involved and the hydrophobicity of the carbon templates.

Recently, hierarchical mesoporous zeolite beta (Beta-H) templated from a mixture of small organic ammonium salts and mesoscale cationic polymers has been reported that possesses dual porosity due to the presence of zeolite nanocrystals forming a mesoporous structure, which provides significantly improved mass transport behavior in alkylation catalysis (Xiao et al. 2006). This route involves a one-step hydrothermal synthesis, and the templated mixture is homogeneously dispersed in the synthetic gel. Importantly, these novel hierarchical zeolites exhibit excellent catalytic properties as compared to conventional zeolite beta. Beta zeolite is generally synthesized from a small organic template of tetraethylammonium hydroxide (TEAOH). Hierarchical mesoporous Beta zeolite (Beta-H) is crystallized in the presence of TEAOH and a mesoscale cationic polymer, polydiallyldimethylammonium chloride (PDADMAC).

Scanning and transmission electron microscopy (SEM and TEM) images of Beta-H (Figure 7.2) reveal the presence of zeolite particles about 600 nm in size and hierarchical mesoporosity in the 5–40 nm range. Partial connections may be observed between these hierarchical pores; these are beneficial for the mass transfer of reactants and products in catalysis. Beta-H showed a high activity and selectivity as an alkylation catalyst (Figure 7.3), as well as a long catalyst life relative to the sample of conventional Beta zeolite. The similarities of Beta-H to conventional Beta zeolite in terms of Si/Al ratios, aluminum distribution, and acidic strength, as well as the larger particle size of Beta-H than that of Beta zeolite indicate that the higher catalytic activity of Beta-H in the model alkylation reaction is related to the hierarchical mesoporosity in Beta-H, which is important for improving the mass transport of the reactants and products in the alkylation of benzene with propan-2-ol.

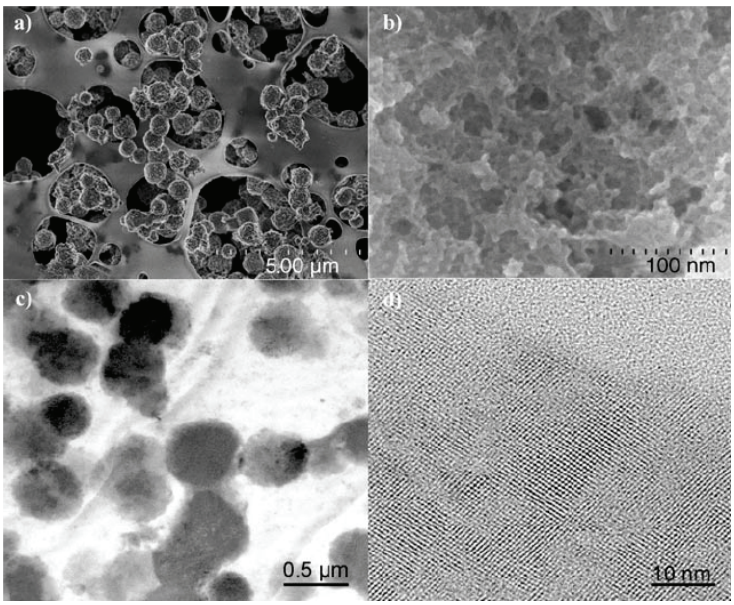

Figure 7.2. Electron microscopy images of calcined Beta-H: (a, b) SEM images at low and high magnification, respectively; the separation between each marker represents 5 µm and 100 nm, respectively); (c, d) TEM images at low and high magnification, respectively (Figure 2 from Xiao et al. 2006).

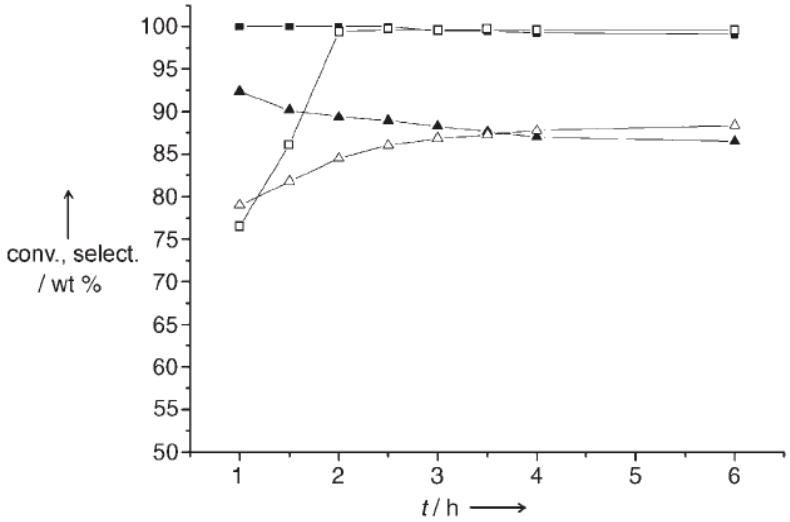

Figure 7.3. Catalytic conversion (conv. [wt %]) and selectivity (select. [wt %]) in the alkylation of benzene with propan-2-ol as a function of reaction time (reaction conditions: 200°C; 4:1 benzene/propan-2-ol; pressure: 2.0 MPa, WHSV: 10 h^{-1}). Conversion on Beta-H (■); selectivity on Beta-H (□); conversion on Beta zeolite (▲); selectivity on Beta zeolite (△). (Figure 3 from Xiao et al. 2006).

The presence of hierarchical mesoporosity in the Beta-H sample is attributed to the use of the molecular and aggregated cationic polymer PDADMAC. The molecular weight of the cationic polymer lies in the range 10^5–10^6, and its size is estimated at 5–40 nm, which is in good agreement with the dimensions of the mesopores obtained from high-resolution TEM studies (Figure 7.2 d). The cationic polymers could effectively interact with negatively charged inorganic silica species in alkaline media, resulting in the hierarchical mesoporosity. The addition of a greater amount of cationic polymer in the synthetic gel yields

Beta zeolite with larger mesoporosity, indicating the controllable mesoporosity of the zeolite sample. The synthesis of hierarchical mesoporous zeolites is not limited to the Beta variety, which was obtained through use of TEAOH with PDADMAC, but other mixtures of organic amine salts and cationic polymer templates may be used if they effectively interact with inorganic species in alkaline media under conditions to crystallize the zeolites. For example, hierarchical mesoporous ZSM-5 zeolite (ZSM-5-H) was obtained using a mixture of tetrapropylamine hydroxide and dimethyldiallyl ammonium chloride acrylamide copolymer (10 wt %). Particularly, the use of the hierarchical mesoporous ZSM-5-H in the catalytic cracking of 1,3,5-triisopropylbenzene showed that it is much more active a catalyst than conventional ZSM-5 under the same reaction conditions (Xiao et al. 2006).

The WTEC team visited the group of Avelino Corma at the Institute of Chemical Technology (Instituto de Tecnología Química or ITQ) in Valencia, Spain. This group has reported novel ultra-large-pore silicogermanate zeolite ITQ-33, which exhibits straight large pore channels with circular openings of 18 rings along the c-axis interconnected by a bidirectional system of 10-ring channels, yielding a structure with very large micropore volume (Figure 7.4, left; Corma et al. 2006; see also ITQ site report in Appendix D). Although the synthesis conditions of ITQ-33 are easily accessible, they are not typical for silicogermanate zeolite analogs and were identified using high-throughput synthesis techniques. ITQ-33 possesses the surface acidity capable of catalyzing with very high-activity, interesting catalytic reactions, such as alkylation of benzene with propylene to produce the industrially relevant cumene, while giving an extremely low yield of the undesirable n-propylbenzene (below 0.01% yield at 99% conversion). When working at very low contact time (weight hourly space velocity or WHSV = 12 h^{-1}), ITQ-33 decays much more slowly than the Beta zeolite commercially used at present (Figure 7.4, right). Activity is maintained after at least five reaction regeneration cycles (540°C in air). ITQ-33 is very active for alkylation and transalkylation of alkyl aromatics, as well as for dealkylation of bulky alkylaromatics containing one or two condensed aromatic rings.[5]

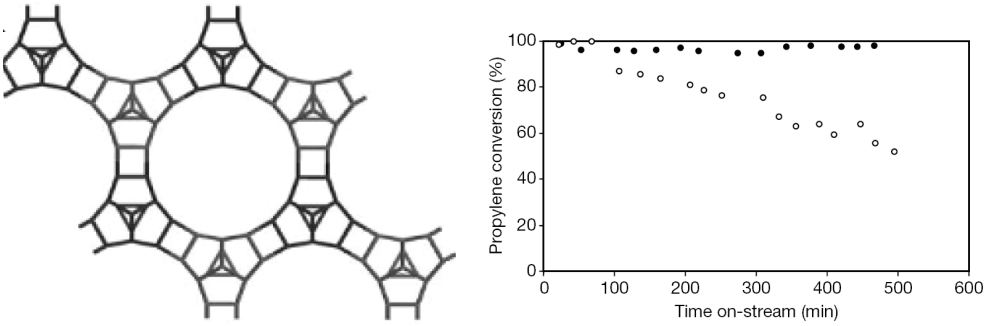

Figure 7.4. (*Left*) view of the ITQ-33 structure along [001], showing the 18-ring structure (oxygen atoms have been removed for clarity); (*Right*) percentage propylene conversion as a function of time on-stream for ITQ-33 and Beta; ITQ-33 is represented by filled circles; Beta is represented by open circles. T=1250C; P=3.5 MPa; WHSV=12 h-1; the benzene/propylene molar ratio is 3.5. (Corma et al. 2006, figures 3 [part] and 4, respectively).

ITQ-33 is of interest for producing more diesel and less gasoline while maintaining the propylene and butene yield, during catalytic cracking of vacuum gasoil. This issue is of importance, given that diesel has higher mileage efficiency than gasoline and given the growing imperative to save fuel and restrict CO_2 emissions. This predicted catalytic behavior would be a consequence of the very large pores that should increase the diesel yield, and the existence of the 10-ring connecting pores that allow diffusion and cracking of gasoline molecules, producing C_3 and C_4 olefins. ITQ-33 gives a cracking conversion higher than Beta and close to that of a USY (ultrastable Y) zeolite. Furthermore, ITQ-33 produces more diesel, less gasoline and propylene/propane, and isobutene/isobutene ratios much higher than does USY, and very similar to results for Beta zeolite. Used together, ITQ-33 and ZSM-5 have an excellent cooperative effect, giving a much higher diesel and propylene yield, with lower gasoline yield, than does the combination of USY and ZSM-5

[5] In summarizing work performed abroad, the author has used some of the groups' own descriptions of their work.

zeolites used today. Zeolite ITQ-33 may thus transform the field of zeolite catalysis, if its stability and economics can be further improved.

The Corma group has demonstrated that it is possible to synthesize amorphous microporous molecular sieves with different pore dimensions and topologies predefined by the size and shape of the organic structure-directing agent (Corma and Díaz-Cabañaz 2006). From the energetic diagram for the different steps occurring during the synthesis of zeolites (Figure 7.5), it appears possible to synthesize in an analogous way stable amorphous microporous molecular sieves with pore dimensions predefined by the size and shape of the organic structure directing agent. These synthesis steps are (a) an induction period, (b) nucleation, in which viable nuclei are formed, and (c) growth of the nuclei to form zeolite crystals. Following the reaction steps given in Figure 7.5, the Corma group synthesized and isolated, before nucleation occurred, stable amorphous microporous materials. These new microporous stable materials can be considered as amorphous zeolite precursors (ZP) containing zeolitic nuclei that are too small to show crystallinity by different spectroscopic techniques. These novel nanosized zeolitic materials have several advantages over conventional zeolites, i.e., they can always be obtained in high yields, with shorter synthesis times, and in larger compositional ranges.

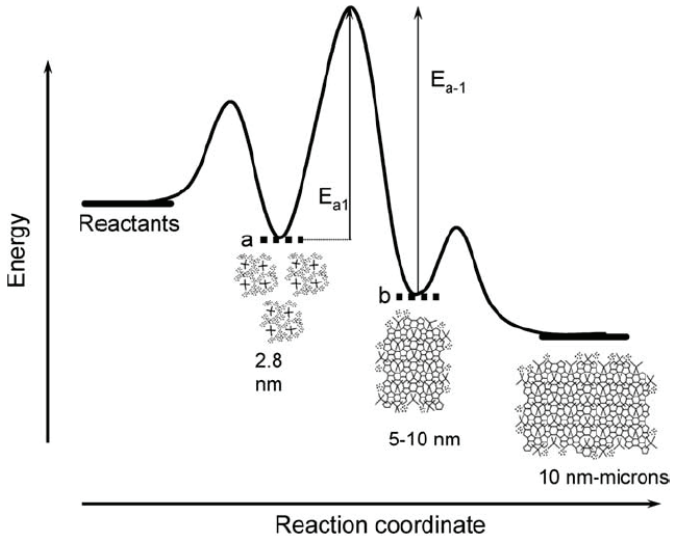

Figure 7.5. Energetics of zeolite crystallization (Fig. 1 from Corma and Díaz-Cabañaz 2006).

Corma and Díaz-Cabañaz also reported ZSM-12 (monodimensional 12-ring channel), NU-87 (bidimensional 10-ring pore), and ITQ-21 (three-dimensional 12-ring channels) zeolite precursors that possessed micropore diameters and pore volumes similar to corresponding well-crystallized zeolites. These zeolite precursors correspond to partially arranged amorphous versions of the zeolite with already a large amount of Si–O–Si bonds formed, but with still an important fraction of internal defects, as was evidenced by ^{29}Si MAS NMR. ^{27}Al MAS NMR showed that Al in calcined zeolite precursors is in tetrahedral coordination and accounts for the Brønsted acidity observed by pyridine-adsorption/desorption measurements. These acid sites are active and selective for catalyzing alkylation and cracking reactions of hydrocarbons. The catalytic results show that the microporous amorphous molecular sieve ZPITQ-21 gives the same catalytic activity as the corresponding large pore zeolite (12-R) ITQ-21 for cracking 1,3-diisopropylbenzene (DIPB), which can easily diffuse into 12-ring pore zeolites. However, for cracking the bulkier 1,3,5-triisopropylbenzene (TIPB), ZPITQ-21 is more active than ITQ-21, showing the presence of slightly larger pores, probably due to incompletely formed cages and cavities in the former material. The above observation is consistent with the distribution of the trimethylpentane isomers (TMP) obtained during alkylation of 2-butene with isobutane. ZPITQ-21 is more selective towards the bulkier 2,2,4-TMP and 2,2,3-TMP (which have the highest octane numbers) than the corresponding ITQ-21. It has to be remarked that the molar ratio R (R = (2,2,4-TMP + 2,2,3-TMP)/(2,3,4-TMP + 2,3,3-TMP)) has been associated with shape selectivity effects in zeolites, this ratio being higher for zeolites with larger pores.

DEHYDROGENATION AND HYDROGENATION

There are a number of significant developments related to synthesis and application of novel metal nanoparticle and other nanostructured catalysts in two broad classes of heterogeneously catalyzed organic reactions, dehydrogenation and hydrogenation. A wide spectrum of both dehydrogenation and hydrogenation reactions is catalyzed by noble metal catalysts (e.g., palladium [Pd] and platinum [Pt]) dispersed on metal oxide supports, whereas dehydrogenation reactions, including *oxidative* dehydrogenation reactions (ODH), are also catalyzed by supported transition metal oxides, such as vanadium pentoxide (V_2O_5), molybdenum trioxide (MoO_3), and chromic acid (Cr_2O_3).

Dehydrogenation

Recently, the Somorjai group at the University of California, Berkeley, demonstrated that the rate of cyclohexene hydrogenation and dehydrogenation is influenced by the symmetry of the platinum single crystal faces (McCrea and Somorjai 2000). They concluded that the maximum turnover rate of hydrogenation appeared at lower temperature than the dehydrogenation, and the maximum hydrogenation rate was higher on Pt (111) while lower on Pt (100) faces compared to the rate of dehydrogenation. The phenomenon was traced back to the difference of reaction mechanisms on the two different surfaces and serves as an excellent test reaction occurring with different rates over different crystal faces.

The same group reported for the first time the preparation of catalysts with well-defined shaped metal (platinum, gold, silver, etc.) nanoparticles in the pore system of ordered mesoporous silicas. In this method a colloid solution of metal nanoparticles protected by organic molecules is used as template for the synthesis of SBA-15 (Kónya et al. 2002) and/or MCM-41 (Kónya et al. 2003) mesoporous silicates. A novel type of catalyst composed of well-shaped (cubic) metal particles and mesoporous matrix (pore size 7–8 nm) was prepared and characterized by various physico-chemical techniques. The platinum nanoparticles have well-defined shapes, such as cubic, tetrahedral, cubo-octahedral, etc. The cubic particles have (100) faces, the tetrahedral particles display (111) faces, and the cubo-octahedral particles have both type of faces. In the most favored case, the platinum nanoparticles might be embedded in the pores of mesoporous silica structures, such as MCM-41 and SBA-15. The catalysts prepared in this way may mimic the catalytic processes studied in two dimensions in three dimensions.

Such nanostructured catalytic materials confined to cavities and pores of regular nanoscale dimensions are the subject of continuing interest because they have unique size-dependent catalytic properties, which are significantly different than those of the corresponding bulk catalysts (Rupprechter 2007). The group of researchers at the State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, China, which the WTEC panel visited, has demonstrated that Pt nanoparticle catalysts for methylcycloxane (MCH) dehydrogenation may be prepared by a "one-pot" encapsulation into the mesopore channels of ordered mesoporous SBA-15 silica (Chen et al. 2007). The fabrication of metallic Pt nanoparticles with controllable size and shape has become an important topic in nanotechnology owing to their unique catalytic performance. The use of ordered mesoporous materials as hosts to limit the growth of nanostructured materials in their pores is a highly promising approach to stabilize metal nanoparticles against undesirable aggregation and sintering. Preparation of Pt nanoparticles or nanowires in porous materials typically involves at least two or three steps to restrict Pt nanoparticles in the mesoporous matrix. Chen et al. (2007) developed a novel one-pot approach to directly introduce Pt nanoparticles into the mesochannels of SBA-15, which required no preexisting mesoporous host and Pt nanoparticles, and no extra reduction process of the platinum precursor (Figure 7.6).

This co-assembly method is based on the $I^+M^-S^+$ scheme for the synthesis of mesoporous host (Zhao et al. 1998). The positively charged surfactants such as protonated block copolymers [S^+] and cationic inorganic oxide precursors [I^+] are assembled together through the mediator [M^-]. 3-mercaptopropyltrimethoxysilane [MPTMS] with thiol groups are added to modify the cationic precursors [I+] in order to confine the Pt nanoparticles inside the mesochannels because platinum ions are easy to combined with the thiol groups through strong chemical bonds. The mediator in this case could be the anionic platinum complex and chloride ions.

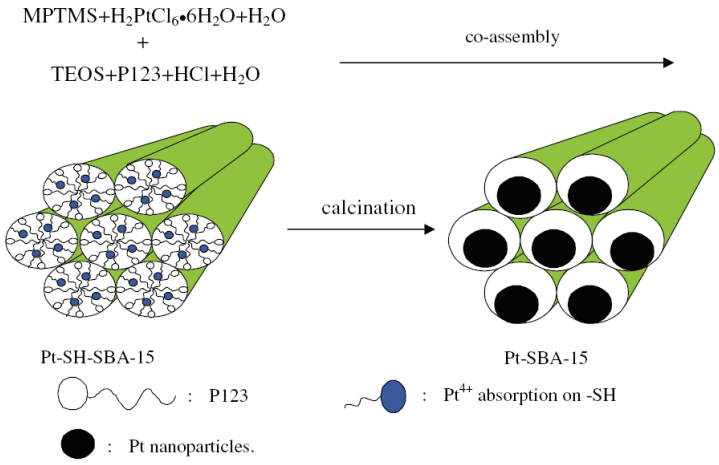

Figure 7.6. Preparation of highly dispersed Pt nanoparticles in the SBA-15 mesochannels (Scheme 1 from Chen et al. 2007).

Figure 7.7 shows the results from the total synthesis route to obtain monodisperse Pt nanoparticles in SBA-15. The direct co-assembly of MPTMS and tetraethylorthosilicate (TEOS) is preferred over the commonly used post synthesis grafting between surface silanols and functional silylation agents, which provides for a more homogeneous distribution of organic ligands in the framework. After adsorption of platinum ions onto the thiol groups, platinum sulfide analogues can be decomposed into metallic platinum and sulfur oxides when heating in air providing a homogeneous distribution of metallic Pt nanoparticles in the mesochannels of SBA-15 after calcination at 550°C to remove the template (Figure 7.6).

These nanocomposites exhibited higher catalytic activity and stability than conventional Pt/SiO_2 catalysts in the methylcyclohexane dehydrogenation (Figure 7.8). All samples showed nearly 100% selectivity to toluene over the entire experimental run. The initial MCH conversion was ca. 65.0% for all catalysts, which then decreased with time on-stream. Pt confined in SBA-15 displayed higher dehydrogenation conversion and stability than that supported on SiO_2 under the same reaction conditions. The smaller particle size and more homogeneous dispersion of Pt in SBA-15 may result in its higher catalytic stability in MCH dehydrogenation as the confinement of ordered mesochannels restricts further growth of Pt nanoparticles during the dehydrogenation reaction.

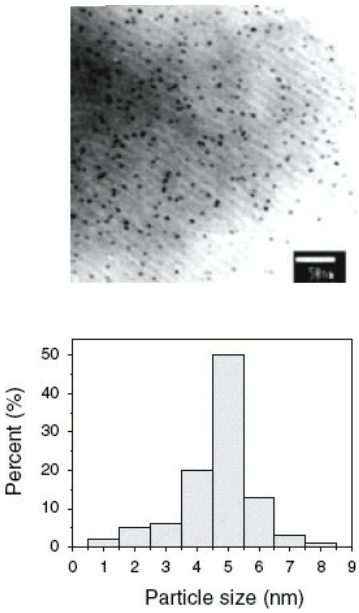

Figure 7.7. TEM images and particle size distribution of Pt–SBA-15 (Figure 5 from Chen *et al.* 2007).

In an ongoing collaboration, the groups of Can Li at the State Key Laboratory of Catalysis of the Dalian Institute of Chemical Physics, China, and Rutger van Santen at Schuit Institute of Catalysis at the Technical University of Eindhoven (see site reports in Appendixes C and D), investigated Fe substitution into the inorganic walls of SBA-15 (Li et al. 2008; Guan et al. 2007; Li et al. 2007). They determined that Fe location had a strong influence on the selectivity to dehydrogenation and dehydration of ethanol. At low Fe loading, Fe was present as isolated species in the amorphous SBA-15 silica and formed aggregated clusters of iron oxide at high Fe loading. The isolated Fe species possessed Brønsted acidity that resulted in selective formation of ethylene, whereas the Fe clusters were efficient in the formation of ethylene and acetaldehyde.

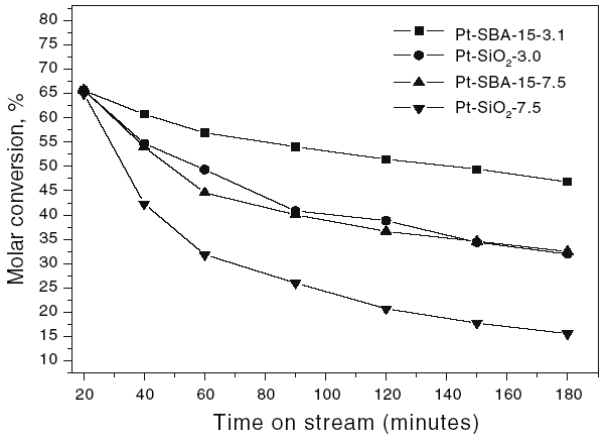

Figure 7.8. Methylcyclohexane conversion by Pt–SBA-15 and conventional Pt–SiO_2 catalysts at atmospheric pressure, 300°C and WHSV of 27.1 as a function of time on-stream (Figure 6 from Chen et al. 2007).

Besides dehydrogenation catalysis, the same collaborators (Zhang et al. 2007) explored further the use of SBA-15 as a catalytic support to prepare a novel interfacial hybrid epoxidation catalyst by a new immobilization method for homogeneous catalysts. Their approach involved coating SBA-15 support with an organic polymer film containing active sites. The titanium silsesquioxane (TiPOSS) complex, which contains a single-site titanium active center, was immobilized successfully by *in situ* copolymerization on a mesoporous SBA-15-supported polystyrene polymer. The resulting hybrid materials exhibit attractive textural properties, such as highly ordered mesostructure, large specific surface area (>380 m^2g^{-1}) and pore volume ($\geq$0.46 cm^3g^{-1}), and high activity in the epoxidation of alkenes. In the epoxidation of cyclooctene with *tert*-Bu hydrogen peroxide (TBHP), the hybrid catalysts have rate constants comparable to that of their homogeneous counterparts and can be recycled at least seven times. These immobilized catalysts can also catalyze the epoxidation of cyclooctene with aqueous H_2O_2 as the oxidant. In two-phase reaction media, the catalysts show much higher activity than their homogeneous counterparts due to the hydrophobic environment around the active centers. They behave as interfacial catalysts due to their multifunctionality, i.e., the hydrophobicity of polystyrene and the polyhedral oligomeric silsesquioxanes (POSS), and the hydrophilicity of the silica and the mesoporous structure. The simultaneous immobilization of homogeneous catalysts on two conventional supports (inorganic solid and organic polymer) has been shown to provide novel heterogeneous catalytic ensembles with attractive textural properties, tunable surface properties, and optimized environments around the active sites.

Several novel synthesis approaches to surface immobilization of homogeneous catalysts in porous or high surface area supports (Figure 7.9) have been reported by the Iwasawa group at the University of Tokyo (Tada and Iwasawa 2006; see also site report, Appendix C). Interfacial chemical bonding of Pd monomers with Pd–P (P: $P(O–iPr)_3$, PMe_2Ph, and dppf) and Pd–N (N: tmeda, methylpiperidine, and cyclohexylamine) to SiO_2, Al_2O_3, and TiO_2 surfaces was employed to obtain a series of supported Pd complex catalysts for the hydroamination of 3-amino-propanol vinyl ether. The order of the hydroamination activities observed for these catalysts correlated with the pKa values of the SiO_2, Al_2O_3, and TiO_2 surfaces. The most ionic bond, Pd–OSi, was favorable for the hydroamination of alkenes, while the Pd–OAl bond with relatively more covalent character did not efficiently promote the reaction. These results show that the chemical bonding with surfaces has a major impact on catalytic activity, and the nature of the support is an important parameter that can be explored to produce new catalytic behavior.

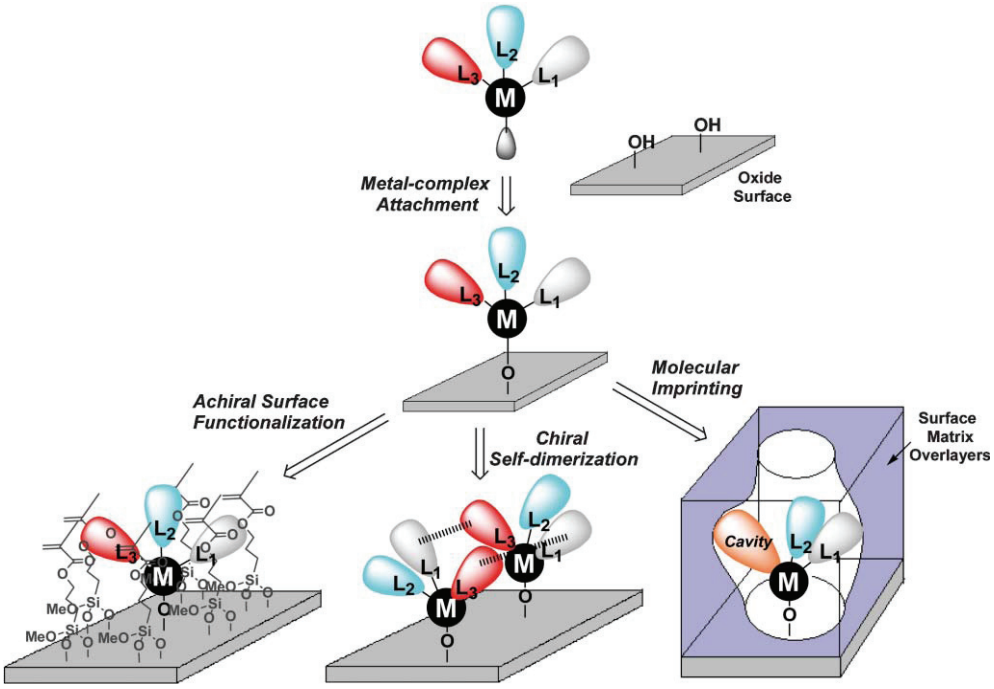

Figure 7.9. Methods for advanced surface design with supported metal complexes (Figure 1 from Tada and Iwasawa 2006).

The Iwasawa group, which the WTEC panel visited at the University of Tokyo, discovered chiral self-dimerization of supported vanadium complexes on a SiO_2 surface, which is a novel phenomenon for metal complexes on oxide surfaces. Two V-monomer complexes with Schiff-base ligands spontaneously dimerized via a selective reaction with a surface Si–OH group, and the formed V dimer had a unique chiral conformation, which is highly enantioselective for the asymmetric oxidative coupling of 2-naphthol with 96% conversion, 100% selectivity to 1,1'-binaphthol (BINOL), and 90 ee%. This surface complex is the first heterogeneous catalyst for the asymmetric coupling reaction, whereas the V monomer is inactive for the oxidative coupling. Another technique reported by the Iwasawa group, surface functionalization of the SiO_2 support with achiral 3-methacryloxypropyl-trimethoxysilane, remarkably amplified the enantioselective catalysis of SiO_2-supported Cu–BOX complexes for asymmetric Diels–Alder reaction. BOX (bis(oxazoline)) is one of the practical ligands for asymmetric catalysis. Enantioselectivity for Diels–Alder reaction can be significantly regulated by surface functionalization with achiral silane-coupling reagents on SiO_2-supported Cu–BOX complexes.

Molecular imprinting methods have recently showed significant promise in creating template-shaped cavities with memory of template molecules that are reminiscent of artificial enzymes possessing recognition ability for particular substrate molecules (Katz and Davis 2000). Acid–base catalysts and metal complexes synthesized by molecular imprinting techniques provide promising molecular recognition catalysis with 100% selectivity for a variety of catalytic reactions where natural enzymes cannot be employed (Tada and Iwasawa 2006).

Molecular imprinting typically consists of several steps: (1) attachment of a metal complex on robust supports, (2) surrounding of the metal complex by a polymer matrix, and (3) production of a shape selective cavity on the metal site in the matrix. Most of the imprinted metal-complex catalysts have been prepared by imprinting in bulk polymers, which discourages the access of reactant molecules to the active sites in the bulk. Moreover, polymers tend to be unstable in organic solvents or under demanding catalytic conditions, such as in the presence of oxidants, at high temperatures, etc. To overcome these limitations, the Iwasawa group designed molecular-imprinted catalysts for oxide-supported metal complexes to produce shape-selective reaction sites by using a ligand on a metal center as a template. A ligand of a supported metal

complex not only influences its catalytic activity but also provides an unsaturated, reactive metal site with a ligand-shaped space after removal of a ligand.

The Iwasawa group chose a ligand of the attached metal complex with a similar shape to a reaction intermediate (half-hydrogenated alkyl) of alkene hydrogenation as a template. This strategy to design active and selective catalysts was based on the following five factors for regulation: (1) conformation of ligands coordinated to a rhodium (Rh) atom, (2) orientation of vacant site on Rh, (3) cavity with complementary molecular shape for the reaction space produced after template removal, (4) architecture of the cavity wall, and (5) micropore in inorganic polymer-matrix overlayers stabilizing the active species at the surface. A $P(OCH_3)_3$ ligand was used as a template with a similar shape to one of the half-hydrogenated species of 3-ethyl-2-pentene, which can produce the template (reaction intermediate)-shaped cavity after extraction of the ligand.

The Iwasawa group succeeded in preparing Rh monomer and a pair of Rh monomers by using appropriate precursors on the surfaces. On both surfaces, $Si(OCH_3)_4$ was deposited by chemical vapor deposition and converted into SiO_2-matrix overlayers surrounding the attached Rh complexes via a hydrolysis–polymerization step. Finally, the template ligand, $P(OCH_3)_3$, was extracted from the attached Rh complex in the SiO_2-matrix overlayers yielding the molecularly imprinted Rh-monomer and Rh-dimer catalysts. The homogeneous complexes, $Rh_2Cl_2(CO)_4$ and $RhCl(P(OCH_3)_3)_3$, and the supported species, $Rh_2Cl_2(CO)_4/SiO_2$, showed no activity for alkene hydrogenation at 348 K. On the other hand, the molecular-imprinted catalysts exhibited significant catalytic hydrogenation activities under similar reaction conditions. For example, hydrogenation of 2-pentene on the molecularly imprinted Rh-dimer catalyst was promoted 51 times as compared to that on the supported catalyst. The metal–metal bonding and coordinative unsaturation of the Rh dimer are key factors for the remarkable activity of the imprinted Rh-dimer catalyst. The selectivity for the alkene hydrogenation on the molecularly imprinted catalysts depended on the alkene size and shape which should come into the reaction site in a template cavity in addition to the electronic and geometric effects of the ligands.

The location of the Rh center for alkenes coordination, the conformation of the remaining $P(OCH_3)_3$ ligand, the orientation of the template vacant site on Rh, the template-shaped cavity, the architecture of the cavity wall, and the micropore surrounding the Rh dimer in the SiO_2-matrix overlayers provided active imprinted catalysts for the size- and shape-selective alkene hydrogenation. Therefore, the arrangement of active sites on surfaces by chiral self-dimerization, surface functionalization with achiral reagents, and molecular imprinting provide new powerful approaches for the design of selective catalyst surfaces in three dimensions beyond conventional homogeneous and heterogeneous catalyst systems.

Hydrogenation

The use of well-defined metal nanoparticles (1-10 nm) for catalytic processes is a rapidly growing area (see recent reviews by Astruc et al. 2005; Chandler and Gilbertson 2006; Tsuji and Fujihara 2007; and Andres et al. 2007). Similar to molecular complexes, metal nanoparticles are efficient and selective catalysts for hydrogenation of olefins and C-C couplings, but also for reactions that are not catalyzed or are poorly catalyzed by molecular species, such as hydrogenation of arenes. However, despite impressive progress in asymmetric catalysis, few colloidal systems have been found to display an interesting activity in this field. Those systems that show promise include Pt(Pd)/cinchonidine for the hydrogenation of ethyl pyruvate and Pd-catalyzed kinetic resolution of racemic substrates in allylic alkylation.

Metal nanoparticle catalysts can be obtained by a variety of methods according to the organic or aqueous nature of the media and the stabilizers used (e.g., Andres et al. 2007). Poly(vinyl)pyrrolidone, PVP, has been the homopolymer most used as stabilizing agent for metallic nanoparticles. Others like cellulose and polysaccharide, polyvinylalcohol, polystyrene, polyacid or poly(vinyl)formamide derivatives, and copolymers and various dendrimers have been also applied for similar purposes. Side-chain functionalized polymers for their applications as stabilizers of metallic nanoparticles are particularly attractive, because the functional groups can interact with the metallic surface (Favier et al. 2007). Favier and colleagues functionalized poly(methyl vinyl ether-co-maleic anhydride) and employed it to stabilize ~3-20 nm sized Pd,

Pt, and Rh nanoparticles, which were investigated in catalytic hydrogenation of ethyl pyruvate (Rh nanoparticles) and C-C coupling using phenylboronic and 2-methylnaphthyl-1-yl boronic acids (Pd nanoparticles). The Rh nanoparticle catalysts employed in the hydrogenation reaction were significantly more active than the conventional heterogeneous Rh catalyst and resistant to agglomeration and sintering.

However, organic polymers are not very stable at high temperatures, and the catalytic reactions in solution may be accompanied by some swelling, which can cause significant mass-transfer resistances. Therefore, the use of inorganic supports or porous hosts appears to be more suitable. Pârvulescu et al. (2006) reported SiO_2-embedded Pd, Au, and highly alloyed Pd–Au colloids prepared by sol–gel embedding of presynthesized colloids and their performances in the hydrogenation of several substrates: cinnamaldehyde, 3-hexyn-1-ol, and styrene. These data showed evidence that alloying Pd with Au in bimetallic colloids leads to enhanced activity and most importantly to improved selectivity. Moreover, the combination of the two metals resulted in catalysts that were very stable against poisoning, as was observed for the styrene hydrogenation in the presence of thiophene.

An interesting example of metal nanoparticle systems prepared by chemical vapor deposition of volatile metal organic precursors into the large pores of metal organic frameworks (MOF) has been reported by Hermes et al. (2005). Hermes and coworkers synthesized several metal@MOF systems in which Cu and Pd nanoparticles were grown inside the pores of MOF-5 framework and were found to be active catalysts for methanol production from syngas (Cu@MOF-5) and cyclooctene hydrogenation (Pd@MOF-5), whereas in the case of the Au@MOF-5 system, Au atoms migrated from the pore cavities of MOF-5 to the external surface and aggregated into large 20 nm Au particles, which were inactive in CO oxidation.

Crooks and colleagues at the University of Texas at Austin and Texas A&M University recently investigated a particle size effect for hydrogenation over unsupported Pd nanoparticle catalysts in a size range (1.3–1.9 nm) that has not been widely studied and demonstrated that the rate of hydrogenation of allyl alcohol is a function of the diameter of the Pd nanoparticles (Wilson et al. 2006). Furthermore, kinetic data indicated that this effect is probably electronic in nature for particles having diameters <1.5 nm, but for larger particles it depends primarily on their geometric properties. The Crooks researchers employed dendrimer-encapsulated nanoparticles (DENs) prepared using dendrimer templates that exert a high degree of control over the size, composition, and structure of catalytically active nanoparticles in the <3 nm size range. Specifically, sixth-generation, hydroxyl terminated polyamidoamine dendrimers (G6-OH) were used to synthesize Pd DENs containing an average of 55, 100, 147, 200, or 250 Pd atoms (G6-OH [Pd_n]), where n is the average number of atoms per particle).

Alkene hydrogenation occurs via the Horiuchi-Polanyi mechanism, which involves dissociative adsorption of H_2 onto the catalyst surface, followed by stepwise hydrogenation of the C=C double bond (Horiuchi and Polanyi 1934). Figure 7.10 shows that only the total number of face atoms increases with particle size, while the numbers of surface and defect atoms both decrease. Differences in reaction rates as a function of catalyst size arise from either electronic or geometric effects. For example, as the size of a nanoparticle decreases, its electronic properties change from those of a metal to an insulator and then to something akin to those of a molecule, which modulate the catalytic properties of nanoparticles. Geometric effects are most evident when a reaction requires a specific type of surface atom, because the ratio of defect (vertex and edge) to face atoms changes dramatically as a function of size for <5 nm diameter particles. While geometric effects have been observed for homogeneous colloidal Pd catalysts for both the Heck and Suzuki coupling reactions, literature reports pertaining to size effects in hydrogenation reactions focus almost exclusively on supported (heterogeneous) Pd catalysts (Wilson et al. 2006).

There is a major conceptual difficulty in that, in the size range where the *electronic* structure of metal particles is changing, there are also major changes in the *geometric* arrangement of atoms on the surface (Bond 2005; Bond et al. 2006; Bond 2007). Therefore, it is impossible to assign the catalytic effects of particles of size less than ~5 nm unambiguously to either a geometric or an electronic effect. However, if the size effect persists for metal particles larger than 5 nm, it is more likely due to a requirement of a specific active site, since the changes in electronic structure become insignificant for such larger particles.

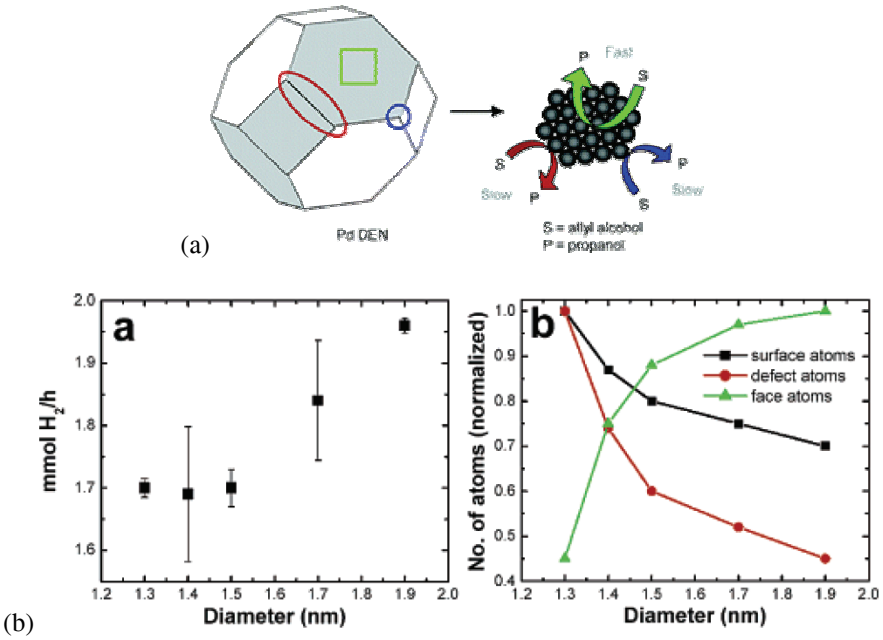

Figure 7.10. (a) Plot of the rate of hydrogen consumption as a function of particle diameter. (b) Plot of the numbers of surface, defect, and face atoms for each particle size. The data are normalized to the largest number of each type of atom (Figure 1 from Wilson et al. 2006).

In addition to catalyst size, the preparation and structure of nanoparticles are also important factors that must be taken into account when comparing catalytic activity. This is because preparation methods, stabilizing ligands, and polydispersity can lead to activity changes that may mask true particle size effects. For example, Pd nanoparticles having similar diameters, but stabilized by either poly(vinylpyrrolidone) or 1,10-phenanthroline, exhibit very different catalytic activities for the hydrogenation of 1,3-cyclooctadiene (Toshima et al. 2001). The hydrogenation reaction is sensitive to both the electronic and geometric properties of the catalytic Pd nanoparticles, both of which change quickly in the 1.3–1.9-nm diameter size range. The hydrogenation kinetics of allyl alcohol (Wilson et al. 2006) are dominated by electronic effects for the smallest particles (<1.5 nm diameter) and by geometric effects for larger particles (1.5–1.9 nm diameter). Results of the type described here were enabled by the high degree of monodispersity resulting from the dendrimer templating approach to nanoparticle synthesis.

The synthesis of particles with narrow size distribution and homogeneous physicochemical properties in order to establish reactivity–morphology relationships is a highly desirable but challenging effort. Controlling the shape at the nanoscale translates into ability to control the relative exposure of different crystal facets and the number of atoms on corners and edges and, hence, ability to tune the activity and selectivity of a catalytic system. The application of shape-controlled synthesis of metallic particles in catalysis is a relatively new direction. However, the number of studies using such catalytic systems has been rapidly growing in recent years. Fukuoka et al. (2001) reported a direct comparison between catalytic properties of spherical and Pt nanowires synthesized inside a mesoporous template. In the hydrogenolysis of butane, Pt nanowires exhibited a 36 times higher turnover frequency than spherical particles. Moreover, Pt nanowires were found to produce ethane by secondary–secondary carbon bond cleavage, whereas spherical Pt particles were able only to cleave to terminal C-C bonds and then to produce methane and propane. This change of catalytic properties was ascribed to the preferential exposure of (110) planes and/or to more electron-deficient sites. Park et al. (2007) reported tetrahedral Rh nanoparticles preferentially exposing the catalytically active (111) planes that were prepared by thermal decomposition of Rh complexes in oleylamine and supported on charcoal. These supported (4.9±0.4) nm Rh particles showed a 5.8- and 109-fold increase in activity for the hydrogenation of anthracene compared to spherical Rh nanoparticles and commercial Rh/C catalyst, respectively.

The catalysis group at the Catholic University of Leuven in Belgium recently reported Au^0 nanocolloids stabilized by polyvinylpyrrolidone (PVP), which displayed high chemoselectivity in the hydrogenation of α,β-unsaturated aldehydes and ketones to allylic alcohols (Mertens et al. 2007). Analogous Pt^0 and Ru^0 nanocolloids were more active than Au^0, but substantially less chemoselective for allylic alcohols. Experimental control over the Au^0 cluster generation provided the opportunity to investigate the size-dependent catalytic behavior of nano-Au^0 and determine the optimum gold cluster size leading to the highest allylic alcohol yields. The optimum cluster size of the Au^0 colloids obtained using $HAuCl_4 \bullet 3H_2O$ as the metal precursor and various PVP/Au ratios was determined for the highest crotyl alcohol yield. At the optimum, the PVP/Au ratio was 6, and based on TEM, nearly spherical Au^0 colloids have a mean diameter of 7 nm.

Telkar et al. (2004) compared the catalytic properties of spherical and cubic Pd particles for hydrogenation of butyne-1,4-diol and of styrene oxide. Very high turnover frequencies were found in both cases using cubic nanoparticles. Moreover, cubic particles were found to be more selective than spherical particles for the hydrogenation of butyne-1,4-diol into but-2-ene-1,4-diol. Similarly, the selectivity in 2-phenyl ethanol for the hydrogenation of styrene oxide was nearly 100% on cubic particles versus less than 50% for conventional catalytic systems. The most detailed study was undertaken by Narayanan and El-Sayed (2004a, 2004b). They used a model reaction, the electron transfer reaction between hexacyanoferrate(III) and thiosulfate ions to study the catalytic properties of cubic, tetrahedral and spherical Pt particles. The particles' reactivity follows the increasing order: cubes < spheres < tetrahedra. The higher reactivity of tetrahedral nanoparticles was related to a higher proportion of corner and edge sites on these particles exposing only {111} faces. Therefore, the morphological control during the synthesis of nanoparticles seems to lead to highly selective catalysts, due to preferential exposure of crystallographic planes. Most of these studies were performed using polymers (polyvinylpyrrolidone, N-isopropylacrylamide, polyacrylate). These organic ligands can modify catalytic properties by affecting the electronic structure of Pt nanoparticles as well as by limiting the accessibility of active sites to reactants and intermediates (Telkar et al. 2004; Sakamoto et al. 2004).

A team of researchers from three French institutions—Institut de Recherches sur la Catalyse et l'Environnement de Lyon, Université Pierre et Marie Curie Paris VI, and Institut Français du Pétrole in Lyon (see site reports in Appendix D)—successfully employed structure-directing agents and a so-called "seeding-mediated" approach to prepare stable and surfactant-free anisotropic Pd nanoparticles (Figure 7.11). These were investigated in selective hydrogenation of buta-1,3-diene (Berhault et al. 2007). In this method, anisotropic growth of nanoparticles is controlled by the selective adsorption of structure-directing agents, e.g., ions, surfactants, or polymers. The selective adsorption of a structure-directing agent inhibits the growth of particles along a given crystallographic direction through a preferential stabilization of specific faces. The polyol process was extensively used to synthesize Group VIIIb noble metal-based nanostructured catalysts. The polyol process uses a polymer as structure-directing agent (generally, PVP), and reduction is performed by the alcoholic solvent. In aqueous media, surfactants (mainly cetyltrimethylammonium bromide, CTAB) play the role of structure-directing agent. Synthesis in aqueous solutions is particularly attractive in the way that (1) surfactant can be eliminated easily from the surface of the nanoparticles and (2) using a "seeding-mediated" approach, the respective rates of nucleation and growth could be better controlled through the injection of seeds serving as unique centers of nucleation-growth at the beginning of the growth process.

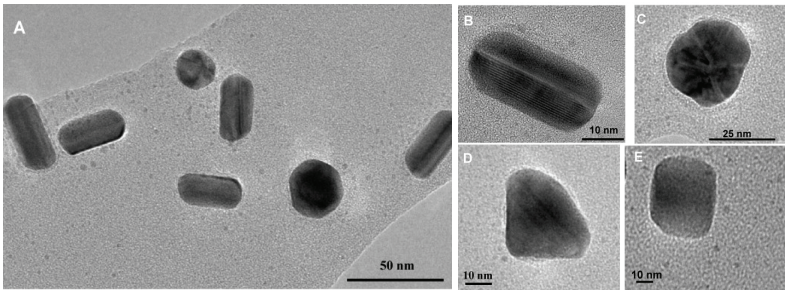

Figure 7.11. TEM images of anisotropic Pd nanoparticles: (A) nanorods and polyhedra; (B) a typical nanorod with a five-fold symmetry; (C) a polyhedron formed from six tetrahedral subunits; (D) a tetrahedral particle with rounded edges; (E) nanocube with rounded edges (Figure 1 from Berhault et al. 2007).

Berhault and coworkers applied this methodology to the synthesis of anisotropic Pd nanoparticles that they employed in the selective hydrogenation of buta-1,3-diene. Selective hydrogenation of unsaturated compounds is a technologically important process in heterogeneous catalysis. Dienes are unwanted by-products of thermal cracking of petroleum cuts. Depending on the target objective, buta-1,3-diene should be converted selectively into but-1-ene in the course of the production of polymers, or into but-2-ene for producing petrochemicals (higher olefins, alcohol), or into gasoline of high octane number after alkylation. Palladium-based catalysts are frequently used for the selective hydrogenation of buta-1,3-diene. This reaction is structure-sensitive, and studies on model catalysts have shown that Pd (110) exhibits a higher selectivity for the formation of butenes than Pd (111) (Silvestre-Alberto, Rupprechter, and Freund 2005; Katano et al. 2003). Similarly, Guo and Madix (1995) have also observed that Pd (100) surfaces are particularly selective for the hydrogenation of dienes into alkenes without further hydrogenation into alkanes.

Berhault and coworkers successfully applied a seeding-mediated approach to synthesize well-defined morphological Pd nanoparticles (nanocubes, nanotetrahedra, nanopolyhedra, and nanorods) using cetyltrimethylammonium bromide (CTAB) as both capping and structure-directing agent (Figure 7.12). Pd nanorods were found to expose preferentially (100) lateral planes due to the selective inhibition by CTAB of the crystalline growth of {100} facets. After deposition onto α-Al_2O_3, these nanostructured Pd particles were tested in the selective hydrogenation of buta-1,3-diene at 298 K under 20 bars of H_2. As compared to an isotropic Pd catalyst, anisotropic Pd catalysts were found to be highly selective for the hydrogenation of buta-1,3-diene into butenes without further hydrogenation into butane. Moreover, further hydrogenation of but-1-ene into butane over these nanostructured catalysts was reduced, whereas but-2-enes were hardly converted. This would be related to the higher exposition of {100} facets on the Pd nanorod catalyst in the absence of any selective poisoning effect due to CTAB. Finally, an unusually high level of *cis* but-2-ene isomer was observed, suggesting a modification of the mechanism usually accepted for Pd catalysts when a well-defined nanomorphology is achieved. The mechanism for the hydrogenation of buta-1,3-diene on the nanostructured catalysts differs from the one generally assumed on "more classical" isotropic catalysts with a higher *cis/trans* but-2-ene ratio, probably resulting from an interconversion between *syn* and *anti* di-adsorbed butadiene species (Figure 7.12). Therefore, nanostructured Pd catalysts present interesting and new catalytic properties differing considerably from the conventional isotropic catalysts. They are also useful model catalysts in order to bring new mechanistic information for selective hydrogenation reactions under relevant experimental conditions.

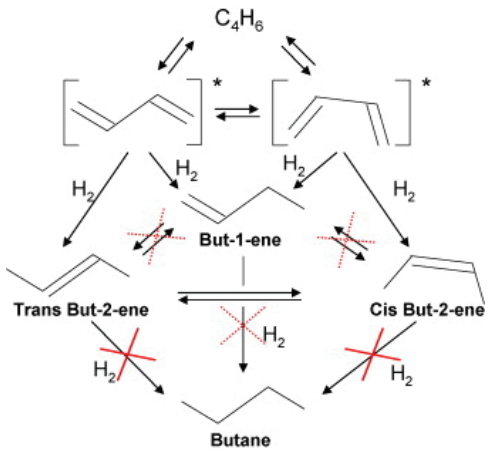

Figure 7.12. Proposed reaction network for buta-1,3-diene hydrogenation on the nanostructured Pd catalysts. The dotted crosses indicate unfavorable routes for the nanostructured Pd catalysts as compared to the isotropic catalyst, whereas solid crosses indicate prohibited routes (Scheme 1 from Berhault et al. 2007).

SELECTIVE OXIDATION

Selective oxidation processes represent a large class of organic reactions where the development of clean and efficient "green chemistry" processes can have a significant positive economic and environmental impact to mitigate the accumulation of greenhouse gases in the atmosphere and other environmental concerns resulting from the world's growing consumption of fossil fuels and current fuel processing techniques. Selective oxidation processes leading to chemical intermediates and fine chemicals have up to now largely relied on stoichiometric reactions employing chromate, permanganate, and renate species. Simple catalytic reactions making use of molecular oxygen or hydrogen peroxide that require minimal energy and produce minimal by-product waste are highly desirable in order to replace stoichiometric reactions that are expensive and environmentally unfriendly.

Selective Oxidation Catalysis by Nanosized Gold and Other Noble Metals

A key emerging technology that shows great promise in selective oxidation is catalysis by gold and gold-containing nanoparticles and nanoclusters (Ishida and Haruta 2007; Hashmi and Hutchings 2006). Gold was earlier considered to be chemically inert and regarded as a poor catalyst. However, when gold is highly dispersed on metal oxides as small nanoparticles with diameters of less than 10 nm (and preferably in the 1.5-3 nm range), it becomes a highly active oxidation catalyst for many reactions, such as CO oxidation and propylene epoxidation in the gas phase (Haruta 2003). Most recently, polymer-supported gold has also shown great promise as a catalyst for green liquid-phase selective oxidation processes (Miyamura et al. 2007). They achieved higher catalytic reactivity for the polymer-supported catalysts than for gold supported on metal oxides via simultaneous optimization of the support, solvents, and size of gold particles.

Over the last decade, following the pioneering work by Prati and Rossi (1998), much attention also has been paid to the development of liquid-phase oxidation processes employing gold nanoparticle catalysts. The ultimate objective is to carry out green liquid-phase oxidations at atmospheric pressure and room temperature, either in aqueous media or under solvent-free conditions, and using air as oxidant. Gold nanoparticles supported on activated carbon or metal oxides are active for liquid-phase selective oxidation of alcohols and polyols into the corresponding aldehydes, ketones, or carboxylic acid with molecular oxygen in aqueous media (Corma and Serna 2006; Ketchie, Murayama, and Davis 2007). In most cases, gold catalysts showed high catalytic activity with much higher selectivity at lower temperature and stability than palladium and platinum catalysts. The selective oxidation of glucose by gold supported on activated carbon or metal oxides has been a very active research area, as the transformation of readily available glucose to valuable gluconic acid is of great importance (e.g., Comotti et al. 2005). In fact, gold catalysts supported on activated carbon and Al_2O_3 were efficient under moderate conditions (e.g., atmospheric pressure, using molecular oxygen as oxidant, and reaction temperatures of 303–333 K). In the case of Au on activated carbon, turnover frequencies (TOF) reached high values (12,500 to 25,000 h^{-1}), and high selectivities to gluconic acid were observed ranging from 92 to 99% by varying the kind of activated carbon.

Au nanoparticles (2–5 nm) supported on nanocrystalline CeO_2 (ca. 5 nm) gave a particularly active, selective, and recyclable catalyst for the oxidation of alcohols using molecular oxygen at atmospheric pressure under solvent-free and base-free conditions (e.g., Abad et al. 2006). The TOF value for oxidation of 1-phenylethanol (12,480 h^{-1}) exceeded that of Pd nanoparticles supported on hydroxyapatite (9,800 h^{-1}) (Mori et al. 2004). The Au/CeO_2 showed a much higher selectivity for the oxidation of allylic alcohols to unsaturated ketones, e.g., yielding 1-octen-3-one as a main product in the presence of Au/CeO_2 with a selectivity of 93% in the oxidation of 1-octen-3-ol. The Pd/CeO_2 displayed a lower selectivity of 58% because it promoted isomerization and hydrogenation of the C=C bond to yield saturated ketones as a by-product (Abad et al. 2006). Moreover, Au supported on activated carbon and Au/Al_2O_3 preferentially oxidized the hydroxy group in 2-aminopropanol to yield 2-aminopropanoic acid and avoided the oxidation of the amino group (Biella et al. 2002), indicating an attractive chemoselectivity in liquid-phase aerobic oxidations.

Recently, the interest of the catalysis community has shifted from activated carbon and metal oxides to organic polymers as a stabilizing agent or a solid support for gold nanoparticles in liquid-phase oxidations.

Tsunoyama and colleagues (2005) reported that small gold clusters 1.3 nm in diameter stabilized by hydrophilic poly(N-vinylpyrrolidone) (Au:PVP) catalyzed the oxidation of benzyl alcohol into benzaldehyde as the main product and benzoic acid as a by-product in water at 303 K using molecular oxygen as oxidant. They indicated that the TOF value was inversely proportional to the diameter of the Au nanoparticles in the 3–6 nm range and, further, increased significantly for Au nanoparticles smaller than 3 nm. The disadvantage of the Au:PVP system is that the Au catalyst was essentially present as a homogeneous catalyst, which complicates its separation from the reaction medium.

Gel-type polyacrylic resin, poly-2-(methylthio)ethyl methacrylate-N,N-dimethyl acrylamide-N,N-methylene bisacrylamide (MTEMA-DMAA-4–8), was successfully employed to prepare recyclable supported catalysts containing well-defined gold nanoparticles (Burato et al. 2005). The thioether (R-S-R) group was used as a coordination site for a Au precursor prior to its reduction to Au^0 with $NaBH_4$. The gel-type resin had small pores with a mean diameter of 2.5 nm, while the size of the Au nanoparticles was 2.2 nm, suggesting that the cavities in the polymer gel prevented the Au nanoparticles from aggregating. The gold nanoparticles supported on the gel-type polymer catalyzed the oxidation of pentanol to pentanal (25% conversion) and of pentanal to pentanoic acid (95% conversion). These performances, however, were still inferior to that of Au/CeO_2. Miyamura et al. (2007) developed recyclable polystyrene-based copolymer-microencapsulated gold nanocatalysts (PI-Au), in which gold nanoparticles were stabilized by benzene rings in the polystyrene moiety. These PI-Au catalysts were active at room temperature when using the appropriate combination of water, organic solvent, and base. Recently, the Haruta group (see Tokyo Metropolitan University site report, Appendix C) has developed a simple, patented, technique to prepare polymer catalysts by using surface functional groups on an anion-exchange resin as a reducing agent (Ishida et al. 2008). The obtained Au/polymer catalysts exhibit a higher TOF (27,000 h^{-1}) than the Au/activated carbon catalyst the group of Rossi employed in the oxidation of glucose to gluconic acid in water (Comotti et al. 2005).

The Hutchings group at Cardiff University in the UK (see site report, Appendix D) had previously studied solvent effects on the selective oxidation of cyclohexene over Au on activated carbon, where the highest selectivity for cyclohexene oxide (50%) was obtained in 1,2,3,5-tetramethylbenzene, while 2-cyclohexen-1-one was obtained as a main product (78% selectivity) in 1,3,5-trimethylbenzene at 353 K (Hughes et al. 2005). The Kobayashi group at the University of Tokyo has shown that further optimization of reaction media could lead to the use of milder conditions, such as room temperature (Miyamura et al. 2007). They also examined the solvent-free oxidation of 1-phenylethanol at 433 K under almost the same reaction conditions (at atmospheric pressure) as employed by the Corma group (Abad et al. 2006). The TOF value for PI-Au (20,000 h^{-1}) exceeded that for the Au/CeO_2 catalyst (12,480 h^{-1}) reported by Abad et al. 2006.

Functionalized organic polymers are highly promising not only as a support to stabilize small gold nanoparticles but also as promoters of higher catalytic activity as compared to conventional gold catalysts supported on metal oxides and activated carbon. Despite the recent progress, the reaction mechanism involving the functionalized group in the polymer backbone and the size effect of gold nanoparticles both remain unclear. In the case of Au/CeO_2, the proposed reaction mechanism involves cationic gold species and Ce^{3+}, and the oxygen-deficient sites of CeO_2 are assumed to play an important role for physisorption of molecular oxygen. Additionally, the production of small gold clusters with diameters of less than 2 nm, which is a critical size for a dramatic change in electronic structure, is still an emerging and exciting area of research (Bond, Louis, and Thompson 2006). These small clusters composed of less than 300 atoms can be tuned more pronouncedly by choosing support materials ranging from metal oxides and activated carbon to polymers. The success of the Kobayashi group in controlling the size of gold particles down to 1 nm through entrapment in a polymer particle represents an important step toward the goal of sustainable chemistry.

For Au nanoparticles supported on metal oxides, a general synthetic strategy developed by the Stucky group at the University of California, Santa Barbara, to prepare and disperse Au nanoparticles even on acidic and hydrophobic supports appears to be highly promising (Zheng and Stucky 2006). In this method the narrow size distribution of Au nanoparticles is generated by employing weaker reducing agents than the commonly used $NaBH_4$, followed by capping the stable monodisperse Au nanoparticles by long-chain alkyl thiols to yield hydrophobic nanoparticles. A homogeneous loading of capped Au nanoparticles is created by utilizing their weak interactions with oxide surfaces in aprotic solvents, which is then locked in place by calcination to

remove the surface capping groups. Zheng and Stucky reported 3.5–8.2 nm Au particles by selecting different solvents and controlling the reaction temperatures. However, it remains to be seen if this method could be adapted to prepare even smaller Au nanoparticles (< 3 nm in diameter).

Lastly, great success has been achieved in a variety of catalytic processes by combining two metallic elements in bimetallic catalysts, such as the platinum-iridium (Pt-Ir) system for petroleum reforming, platinum-tin (Pt-Sn) for alkane dehydrogenation, and the nickel-gold (Ni-Au) system for steam-reforming of alkanes (Bond 2005). The recent interest in gold as a catalytic element has led to a series of studies on gold-containing bimetallic combinations (Bond, Louis, and Thompson 2006). In particular, the palladium-gold (Pd-Au) system has been found more effective than either component by itself in a number of selective oxidations, including those of reducing sugars, alkenes, and hydrogen (to form hydrogen peroxide rather than water). In the macroscopic state, palladium and gold form a continuous range of solid solutions, and it was expected that chemical methods for preparing nanoscale bimetallic particles would also lead to microalloys. Surprisingly, detailed structural examination has shown that this is not always the case; instead, a core-shell structure often occurs, in which a gold core is surrounded by a palladium shell (Edwards et al. 2005). The beneficial catalytic effect is therefore obtained by the Au core exerting some kind of modifying influence on the surface Pd atoms, which this has not yet received a theoretical explanation.

Intriguing results for bimetallic AuPd catalysts supported on activated carbon in the aqueous-phase oxidation of glycerol have been reported by the Davis group at the University of Virginia (Ketchie, Murayama, and Davis 2007). They prepared bimetallic catalysts by depositing Au from solution onto commercial 3 wt.% Pd/C catalyst. According to EXAFS data, the AuPd catalyst at low Au loading contained Au "skin" on the Pd core, whereas at high Au loading, gold deposited as highly dispersed monometallic clusters on the support. Another bimetallic AuPd was prepared by the Au sol method and gave a catalyst in which Au almost completely covered Pd. However, no significant rate enhancement was found for the bimetallic catalysts compared with monometallic Au after the rates of glycerol oxidation were properly normalized to the surface metal concentration. Pd does appear to have an important influence on the selectivity of the glycerol oxidation reaction. Kinetic studies revealed that Pd in either a bimetallic particle or a physical mixture with Au decreased the H_2O_2 formation in the reaction. Since H_2O_2 is correlated with the formation of C–C cleavage products, the presence of Pd with Au increased the selectivity of the glycerol oxidation to the formation of glyceric acid. These results (Ketchie, Murayama, and Davis 2007; Bond, Louis, and Thompson 2006; Edwards et al. 2005) further suggested that bimetallic and multimetallic Au-based catalysts represent another highly promising and relatively unexplored dimension of Au catalysis in selective oxidation reactions.

Selective Oxidation of Lower Alkanes by Bulk Mixed Metal Oxides

Selective oxidation catalysis is of vital importance to society, providing about a quarter of all organic chemicals and intermediates used to make consumer goods and the industrial products that rely on them (Grasselli 2002). The goal to use less-expensive feedstock materials has spawned the development of new and improved heterogeneous catalysts for C2-C4 conversions. In the selective oxidation and ammoxidation of C3 feedstocks, significant efforts are underway to use propane feeds in processes that produce acrylic acid and acrylonitrile over processes that have traditionally relied on propene feeds catalyzed by promoted (multicomponent) bismuth molybdates for the production of acrolein and acrylonitrile. The production of acrylic acid (currently from acrolein) and acrylonitrile has reached a scale that approaches the equivalent of nearly 1 kg for every human being on Earth each year (Pyrz et al. 2008).

Among various candidate systems investigated for selective (amm)oxidation of propane, the so-called "M1/M2" phase system with the bulk Mo-V-Nb-Te-O composition appears to be the most viable for commercial implementation. This system contains two crystalline phases (M1 and M2); the synergy between them has been claimed to be critical for the achievement of optimal selectivity during propane conversion (Holmberg, Grasselli, and Andersson 2004; Baca et al. 2005). M1 is the majority phase in this catalyst and has an orthorhombic polyhedral network-type molybdenum bronze structure with a framework similar to that of Mo_5O_{14} and related bronzes (Figure 7.13). This phase can be described with the generic formula $\{TeO\}_{1-x}\cdot(Mo,V,Nb)_{10}O_{28}$, where the {TeO} component is intercalated into framework channels.

The M2 phase is optimally present in amounts of roughly 20–30% and is an orthorhombically distorted hexagonal tungsten bronze (HTB)-type structure (DeSanto et al. 2004). In analogy to the generic description of the M1 formula, the formula for M2 can be written as $\{TeO\}_{2-x}\cdot(Mo,V,Nb)_6O_{18}$. This M1/M2 composite is both active and selective, providing up to 62 mol.% acrylonitrile yield in propane ammoxidation. These conversions require a trifunctional active site where the activation of the highly stable paraffin C-H bond on a V(V) site is followed by the abstraction of α-H and a subsequent sacrificial insertion of oxygen (oxidation possibly involving a O=Mo=O species) or nitrogen (ammoxidation requiring co-fed NH_3 that was proposed to adsorb and form O=Mo=NH species) on the catalyst surface (Grasselli 2005). The structural and chemical complexity of the M1/M2 system may provide a site-isolated complex trifunctional active site for selective conversion (Grasselli 2005). The insertion step requires that lattice oxygen be indirectly replenished, and the overall process involves a complex interplay of electrons and protons at the active surface.

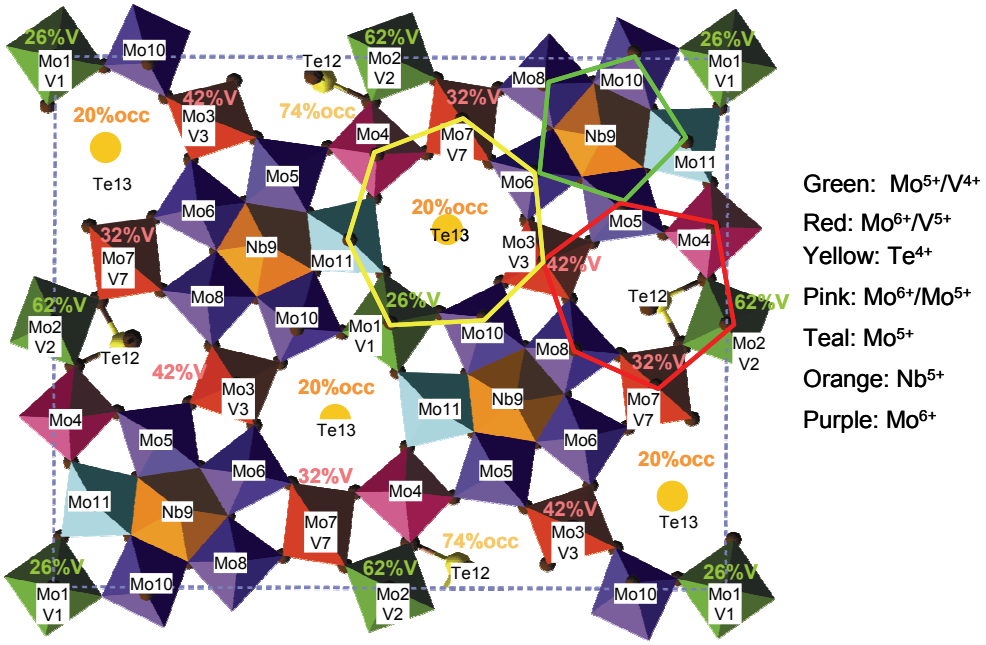

Figure 7.13. Bulk *ab* planes of M1 phase (DeSanto et al. 2004). The refined orthogonal structure had the space group *Pba2*, a formula unit $Mo_{7.8}V_{1.2}NbTe_{0.937}O_{28.9}$, and lattice parameters a = 21.134(2) Å, b = 26.658(2) Å, and c = 4.0146(3) Å with Z = 4 (Figure 1 from Pyrz et al. 2008).

Although the crystal structures of the M1 and M2 phases have been reported (DeSanto et al. 2004), the detailed description of molybdenum (Mo), vanadium (V), and niobium (Nb) locations and their roles in the overall catalytic behavior of the Mo-V-Te-Nb-O system is still rather limited. For instance, although only the M1 phase is able to activate propane, the presence of M2 was shown to improve the selectivity of the M1 phase during propane oxidation to acrylic acid and propane ammoxidation to acrylonitrile (e.g., Holmberg et al. 2004; Baca et al. 2005). The propane ammoxidation to acrylonitrile is proposed to occur via the propylene intermediate, where the M1 phase is responsible for propane oxidative dehydrogenation to propylene and its further ammoxidation to acrylonitrile, while the M2 phase was proposed to be more efficient in propylene ammoxidation to acrylonitrile. However, the cooperation between these two phases in propane ammoxidation is still poorly understood because the M1 and M2 phases employed in these previous studies were often prepared by different synthesis techniques (e.g., slurry evaporation vs. solid-state) and possessed different chemical compositions.

Catalytic Behavior of Mo-V-(Te-Nb)-O M1 Phase Catalysts

The Ueda group (Catalysis Research Center at the University of Hokkaido; see site report in Appendix C) and the Guliants group at the University of Cincinnati recently reported compositionally simpler Mo-V-O,

Mo-V-Te-O, and more complex Mo-V-Te-Nb-O M1 phase catalysts prepared by hydrothermal synthesis (Watanabe and Ueda 2006; Shiju and Guliants 2007). Despite close similarities in the bulk crystal structure and chemical composition, the Mo-V-(Te-Nb)-O catalysts displayed significant differences in catalytic performance in propane ammoxidation to acrylonitrile (Korovchenko et al. 2008). The M2 phases were inactive in propane ammoxidation, whereas the Mo-V-O M1 phase displayed the highest activity among all M1 phases studied but modest selectivity to acrylonitrile that was similar to that of the Mo-V-Te-O M1 phase catalyst. However, the presence of Nb together with Te in the M1 phase resulted in a dramatic drop in the activity in propane and propylene ammoxidation, accompanied by significant enhancement in the selectivity to acrylonitrile.

On Cooperation of M1 and M2 Phases in Propane Ammoxidation

Several groups have reported improvement in the acrylonitrile yield as a result of the cooperation of the M1 and M2 phases in the Mo-V-Te-Nb-O system (e.g., Holmberg, Grasselli, and Andersson 2004; Baca et al. 2005). The presence of up to 40% M2 phase in these catalysts was claimed to improve the acrylonitrile yield due to the ability of this phase to actively and selectively convert the propylene intermediate desorbed from the M1 phase into acrylonitrile. However, these studies were conducted at $\leq$50% propane conversion when significant propylene formation (10–30 mol.% selectivity) over the pure M1 phase catalyst was observed, whereas the selectivity to propylene over the pure M1 phase was typically <4 mol.% at high propane conversion >60% (e.g., Grasselli 2005; Watanabe and Ueda 2006).

In order to elucidate the role of the M1/M2 phase cooperation, propane ammoxidation was conducted over (1) an original $Mo_1V_{0.3}Te_{0.17}Nb_{0.12}$ catalyst containing 75% M1 and 25% M2 and (2) a pure M1 phase obtained from the original catalyst by selective dissolution of the M2 phase in H_2O_2 (Korovchenko et al. 2008). A subsequent elemental analysis of this H_2O_2 solution indicated that the M2 phase formed *in situ* together with the M1 phase in the Nb-containing $Mo_1V_{0.3}Te_{0.17}Nb_{0.12}$ system was essentially Nb-free in agreement with previous observations (e.g., Grasselli 2005). The results of this study conducted at an optimal temperature of 693 K (Figure 7.14) confirmed that the M1+M2 mixture was more efficient in propane ammoxidation at low to moderate propane conversion (<50%) because the Nb-free M2 phase was much more active than the Nb-containing M1 phase in ammoxidation of the propylene intermediate formed over the M1 phase, e.g., the initial rates of ~5 and 0.6 μmol/m_2• s, respectively, at 693 K in $C_3H_6/NH_3/O_2/He$ =6/7/17/70. However, this advantage was lost at longer reactor residence times and higher propane conversion as the M1 phase became more efficient in propylene ammoxidation. Therefore, at high propane conversions important for applied reasons, the M1 phase is *the only crystalline phase required for the activity and selectivity* of the bulk Mo-V-Te-Nb-O catalysts in propane ammoxidation to acrylonitrile.

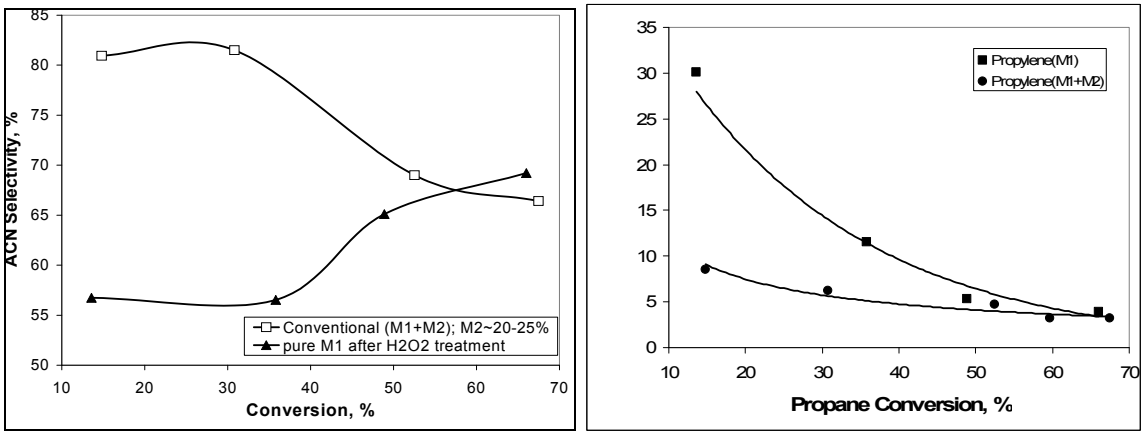

Figure 7.14. Selectivity to acrylonitrile, ACN (left) and propylene (right) for propane ammoxidation at 693 K over (M1+M2) and pure M1 Mo-V-Te-Nb-O catalysts. W_{cat}=0.2g (diluted with 0.5g SiC); F= 20ml/min; Feed composition: $C_3H_8/NH_3/O_2/He$ =6/7/17/70 (Figure 7 from Korovchenko et al. 2008).

Surface Termination of M1 Phase

Recently, the Schlögl group at the Fritz Haber Institute in Berlin (see site report in Appendix D) reported that the *ab* planes in the Mo-V-Te-Nb-O M1 phase terminated with a nanometer-thick disordered layer (Wagner et al. 2006). They concluded that it corresponded to nanoparticles supported on the M1 phase made from a supramolecular network of oxoclusters and containing the active and selective surface sites for propane (amm)oxidation. However, the results of recent high-resolution TEM and low-energy ion scattering (LEIS) studies of the *ab* plane in the M1 catalyst (Korovchenko et al. 2008; Guliants et al. 2005a) provided compelling evidence that the active and selective sites may be associated with a specific surface termination of the M1 phase rather than supramolecular structures (Wagner et al. 2006).

As the LEIS data shown in Figure 7.15 suggest, only the topmost surface displayed the chemical composition different from that in the bulk. Moreover, a study of propane oxidation to acrylic acid over the Mo-V-Te-O M1 phase catalysts indicated that the rates of propane consumption and formation of propylene and acrylic acid depended on the topmost surface V concentration, whereas no dependence of these reaction rates on either the surface Mo or Te concentrations was observed (Guliants et al. 2005a). Average reaction orders of 2.3 ± 0.4, 1.6 ± 0.6, and 3.3 ± 0.6 were found, respectively, for propane consumption, propylene, and acrylic acid formation at 360–450°C with respect to the topmost surface V concentration, suggesting that multiple surface VO_x sites were more efficient in propane activation and formation of acrylic acid over the model Mo-V-Te-O catalysts than the isolated VO_x sites. These results suggest that the surface VO_x is the active and selective species, not only in the initial step of propane activation and ODH to propylene, but also in the subsequent steps of the allylic oxidation of propylene intermediate to acrolein and acrylic acid.

These recent findings suggest further that the M1 phase is the only crystalline phase required for the activity and selectivity of the Mo-V-Te-Nb-O catalysts in propane ammoxidation to acrylonitrile at high propane conversion, whereas a cooperation between the M1 and M2 phases is observed at low propane conversion. High-resolution TEM and LEIS studies indicated that the M1 phase is terminated by a *surface monolayer* proposed to be responsible for its activity and selectivity in propane (amm)oxidation. The experimental evidence is mounting that selective propane (amm)oxidation occurs at the surface *ab* planes of the M1 phase. Multiple VO_x sites present in the surface *ab* planes of the M1 phase were proposed to be highly efficient for this 8-ē oxidation reaction, whereas other surface MO_x species tune the activity and selectivity of the surface VO_x species by forming bridging V-O-M bonds and modifying the surface acidity to control the residence times of the surface intermediates and reaction products.

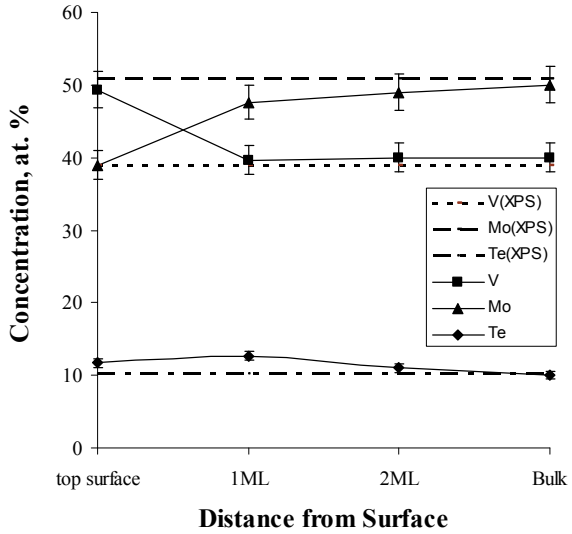

Figure 7.15. Mo, V, and Te concentration profiles in the surface region of the $Mo_{0.3}V_{0.6}Te_{0.1}O$ M1 catalyst (Figure 7 from Guliants et al. 2005a).

From a practical viewpoint, the results of these studies strongly indicate that further synthetic optimization of the topmost surface composition and surface promotion of the M1 phase with metal oxides species to form new surface active V-O-M sites are two highly promising directions to enhance catalytic performance of these mixed metal oxides in propane (amm)oxidation. The M1 phase possesses unique catalytic properties among mixed metal oxides, because it is capable of selectively catalyzing three alkane transformations reactions, namely propane ammoxidation to acrylonitrile, propane oxidation to acrylic acid, and oxidative dehydrogenation of ethane. Therefore, improved understanding of the surface structure–reactivity relationships for this unique model system offers a possibility of not only molecular engineering of such mixed metal oxide catalysts for propane (amm)oxidation, but also fundamentally advancing the field of selective alkane (amm)oxidation over bulk mixed metal oxides.

FUTURE TRENDS

The foregoing review provided recent examples of size-, shape-, structure- and composition-dependent behavior of catalyst nanoparticles employed in alkylation, dehydrogenation, hydrogenation, and selective oxidation reactions of fossil resources to chemicals. Innovation in these areas is largely driven by novel synthesis of (nano)porous and nanostructured catalytic materials.

Several new classes of porous alkylation catalysts have recently emerged: periodic mesoporous organosilicas (PMOs), nanosized zeolites, hierarchical mesoporous zeolites, ultralarge-pore open (super)tetrahedral frameworks, metal organic frameworks (MOF), and amorphous microporous molecular sieves. The primary objective in the synthesis of such porous materials is to obtain stable ultralarge-pore frameworks with desirable acidity, shape selectivity, and improved mass transport characteristics for large organic molecules. Whereas supramolecular templating approaches were successful in introducing mesoporosity into known zeolite structures, the discovery of novel ultralarge-pore frameworks with desirable acidity remains largely a serendipitous process, due to the complexity of zeolite crystallization phenomena in the presence of organic structure-directing agents.

Several theoretical approaches to predicting structure-directing agents on the basis of a geometric and energetic fit to the zeolitic cavity including *de novo* design methods have met with some initial success (Catlow et al. 2003; Lewis 2004). However, these expectations have been tempered by new knowledge that formation of stable zeolite frameworks is ultimately governed on a longer length scale by aggregation of nanosized building units during synthesis (Ramanan, Kokkoli, and Tsapatsis 2004; Kremer et al. 2005; Magusin et al. 2005; Rimer et al. 2006). Therefore, accurate description of nucleation and growth of open frameworks on multiple length scales (from a few Å to several nm) and time scales (up to several hours) is critical to being able to design novel open frameworks. On the other hand, from practical considerations it is highly desirable to predict framework locations of catalytically important heteroatoms, as well as catalytic behavior and stability of new porous structures under relevant experimental conditions. Recent studies show that this work is currently underway, and some first promising results are emerging (e.g., Jorge, Auerbach, and Monson 2005 and 2006; Auerbach, Ford, and Monson 2006).

Noble metal nanoparticles (Pt, Pd, Rh, etc.) have been extensively employed to catalyze a wide range of dehydrogenation, hydrogenation, and selective oxidation reactions of organic molecules. In recent years, nanosized Au and its alloys with other metals, e.g., Pd, have shown tremendous promise as superior catalysts for a wide range of selective transformations. Noble metal nanoparticles have been synthesized by a variety of soft chemistry and vapor-phase methods and deposited on solid supports, both inorganic and polymeric, or stabilized by dendritic polymers in solution. Despite an explosion of research on nanoparticles of Au and other noble metals, fundamental understanding of unique size-dependent catalytic behavior of pure gold and its alloys with other metals, as well as the role of support, is still rather limited.

One reason for this slow progress is that the most interesting Au nanoparticles from the catalysis viewpoint contain several hundred Au atoms, and due to their size, such discrete systems are not fully amenable to accurate but computationally expensive high-level *ab initio* molecular electronic structure methods. Although periodic *ab initio* methods are more expedient, the model of a periodic metallic Au is no longer an accurate representation for catalytically relevant Au nanoparticles in the size range 1.5–3 nm. On the other hand,

experimental description of catalytic Au nanoparticles is also limited, due to polydispersity of Au nanoparticle populations and the difficulty of describing the crystal shape of such small particles. How would one begin to quantify the catalytic roles of various crystal faces, edges, steps, and other defects that may exist on surfaces of such small Au crystallites? Another challenge inherent to such small nanoparticles is their limited stability and rapid coarsening, even under mild conditions of liquid phase catalytic processes at room temperature. Other obstacles that impede both fundamental and practical advances include the poisoning and leaching that these catalysts experience under liquid-phase and solvent-free reaction conditions. Therefore, development of novel approaches to synthesize and characterize stable metal nanoparticles with tightly controlled sizes in the 1–4 nm range is critical to gaining fundamental understanding of such catalytic systems.

In this regard, the work of Üli Heiz at the Technical University of Munich (see site report, Appendix D) is highly promising in terms of generating and soft-landing tightly size-controlled Au and other metal clusters containing up to 100 atoms on well-defined single-crystal surfaces of inorganic supports (Gilb, Arenz, and Heiz 2006). Heiz's group, together with the Landman group at the Georgia Institute of Technology, showed a unique size-dependent catalytic behavior of very small Au_8 clusters in CO oxidation (Yoon et al. 2005). Future advances will depend on being able to expand and tightly control the size of Au and other metal nanoparticles in the range of most interest for heterogeneous catalysis, 300–400 atoms, where the electronic structure is in transition regime from that of a large molecule to that of a metal.

Molecular imprinting approaches attempt to mimic nature in designing heterogeneous catalysts that, akin to enzymes, display catalytic cavity shape complementary to that of reactants or even reaction intermediates. To date, these approaches have been based on the "lock and key" concept of enzymatic catalysis originally proposed by Emil Fischer in 1894, which assumes a static character of an enzyme binding pocket (Fischer 1894). However, while this model explains enzyme specificity, it fails to explain the stabilization of the transition state observed in enzymatic catalysis and has been replaced by a dynamic view of "induced fit" (Koshland 1958), according to which both the enzyme active site cavity and the substrate undergo conformational changes. Despite the awareness of the importance of dynamic behavior of enzymes, a unified description of enzymatic catalysis is still incomplete, and a number of proposals are being discussed (e.g., Schramm 2006). These proposals include *ground state destabilization*, which is accomplished by reducing the reaction entropy change by bringing substrates together in the correct orientation to react; and *stabilization of the transition state*, through lowering the activation energy by, for example., straining the shape of a substrate by binding the transition-state conformation of the substrate/product molecules, so that the enzyme distorts the bound substrate(s) into their transition state form, thereby reducing the amount of energy required to complete the transition. Recent studies have provided new insights into the connection between internal dynamics of enzymes and their mechanism of catalysis via so-called "rate-promoting vibrations," which help facilitate catalysis due to atomic motion within the protein along the reaction coordinate (e.g., Eisenmesser et al. 2005). Therefore, future advances in the molecular design of highly active and selective enzyme mimics are likely to depend on our ability to capture both static and dynamic characteristics of enzyme binding pockets in molecularly imprinted catalysts.

The bulk mixed metal oxides of vanadium, molybdenum, and other transition metals have shown great promise as highly active and selective oxidation catalysts. Despite unique ability of some of these crystalline structures to selectively oxidize small alkanes into more reactive and valuable chemical intermediates, such as the M1 phase for propane ammoxidation to acrylonitrile, fundamental understanding of surface molecular structure-reactivity relationships remains highly limited, due to the structural and compositional complexity of these polycrystalline mixed oxides as well as to the limitations of current experimental methods of surface characterization of such systems under any conditions (ultrahigh-vacuum, *in situ*, during catalysis at high pressure). In this regard, it may be argued that our understanding of these complex oxides, from both the experimental and theoretical perspectives, lags behind our knowledge of better defined zeolite and metal catalyst systems. Therefore, significant opportunities exist to advance fundamental understanding of such systems with the ultimate goal of designing improved catalysts for selective alkane oxidation.

Recent studies have shown that such fundamental advances in understanding of mixed metal oxide catalysts may be possible through combined experimental and theoretical approaches. Improved knowledge of

topmost surface compositions in these complex oxides may come from LEIS and high-pressure XPS studies (Bluhm et al. 2007). However, these experimental techniques provide compositional information that is averaged over all crystal planes present in typically polycrystalline mixed metal oxides. Recent studies have provided some indications that these limitations may be overcome via careful passivation of the catalytic surface, followed by selective exposure of specific crystal planes by simple mechanical crushing of a passivated sample (Trunschke et al. 2006). However, these approaches will only provide the chemical composition of the active surface. New insights into the surface structure in these materials may come from novel *in situ* X-ray absorption techniques (Havecker et al. 2004) and further development of combined chemical probe chemisorption/LEIS methods (Guliants et al. 2006) to study the surface reactivity of various metal oxide sites as well as their spatial arrangement at the surface. Ultimately, theoretical approaches, i.e., quantum theory, guided by experimental insights, may assist in judicious selection of first simple cluster models of the active and selective surface sites present in bulk mixed metal oxides. As we grow confident in these early models, these first steps should be expanded to employ larger and more realistic periodic slab models of the catalytic surfaces and techniques that will enable modeling the reactivity under realistic conditions, e.g., temperatures, pressures, and times (Reuter, Stampfl, and Scheffler 2005). Ultimately, the goal of these studies is to develop our understanding of these complex systems to a point where one is able to accurately predict catalytic behavior of surface structures stabilized by the mixed metal oxide bulk under realistic conditions.

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CHAPTER 8

APPLICATIONS: RENEWABLE FUELS AND CHEMICALS

George Huber

INTRODUCTION

Rising fossil fuel prices, combined with widespread concerns about the environmental effects of fossil fuels, are causing researchers worldwide to develop new ways of producing renewable fuels and chemicals. The field of heterogeneous catalysis will be an integral part of the process; no other scientific discipline is as well positioned to make a long-term impact on our ability to efficiently use our renewable resources. Today, catalysis allows us to convert our raw fossil fuel resources to fuels and chemicals that provide us with inexpensive raw materials that drive our economy. In the future, catalysis will be used to efficiently convert renewable resources into the raw materials and liquid fuels that we need to maintain our high living standard.

On the survey the WTEC panel sent to its hosts prior to its visits, the first question asked: What are the major needs, opportunities, or directions in catalysis research over the next 10- and 20-year time frames? Almost all hosts answered that the major research directions in catalysis have to do with sustainability and conversion of renewable resources (sunlight, biomass) to fuels and chemicals. This question was answered the same way in China, Japan, and in Europe by researchers in academia, industry, and in national labs. In addition, the WTEC panelists observed significant local media coverage related to renewable energy projects in the places we visited, indicating public interest in the work. Figure 8.1 shows how Shell envisions the transition to a sustainable energy economy. The field of catalysis will be integral to this transition, the timing of which depends on how quickly scientists and engineers are able to make key scientific and technical discoveries.

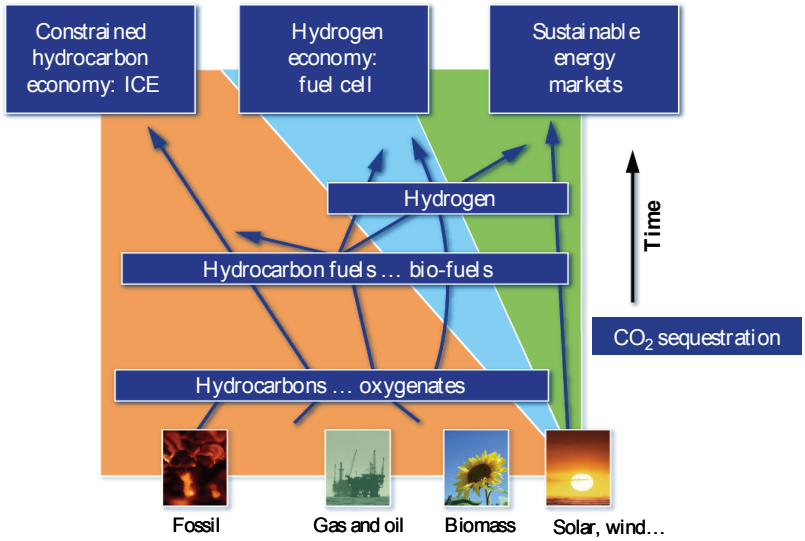

Figure 8.1. The shift from a nonrenewable to a sustainable economy (courtesy of Shell Global Solutions BV).

This chapter assesses the state of the art of catalysis research and development in the United States, Europe, and Asia in the areas of renewable fuels and chemicals, first addressing biomass conversion and then solar energy conversion.

KEY OBSERVATIONS

We are currently seeing an exponential growth in the area of catalysis related to biofuels and renewable energy in both industrial and academic institutions. This is likely to be a critical area for the United States in the next 10 to 20 years as we strive to reduce our dependence on imported oil and nonrenewable fossil energy resources generally. It should be emphasized that the purpose of this WTEC study was not to assess renewable energy, but to assess catalysis research. Therefore, this chapter should not be seen as a summary of worldwide renewable energy research, but as an insight into catalysis research that is being done in relationship to renewable energy.

This study makes six key observations related to catalysis applications to renewable fuels and chemicals:

- Catalysis is the key cross-cutting science that will allow efficient conversion of renewable resources (sunlight, biomass, hydrogen) into fuels and chemicals.
- Many research projects in catalytic biomass conversion are just now getting started; this new area appears to be growing exponentially.
- The United States is not devoting as much resources to catalysis and biofuel projects as many other parts of the world. Europe publishes the greatest number of papers related to biomass conversion with heterogeneous catalysis, especially related to biochemicals and biofuels. However, the papers published in the United States have a higher potential citation impact than those published in Europe.
- Land is available worldwide for renewable energy and biofuels. WTEC panelists were not able to visit a number of countries that are heavily invested in biofuels (Brazil, Canada, etc.).
- Japan is a world leader in photocatalytic splitting of water.
- China and India are rapidly developing industrial biofuel products (furfural, jatropha).

BIOMASS CONVERSION

Biomass Feedstocks

Worldwide, there is a large amount of unused land that could be used to produce biomass, and there is already a large amount of biomass that is available for use as a feedstock to make liquid fuels and chemicals. Most of the existing biomass is in the form of lignocellulosic biomass (e.g., plants in the grass family, trees, and byproducts or waste products associated with their use). This form of biomass is not yet being used as a feedstock for liquid fuels because the technology has not yet been developed. Currently only oil-, sugar-, and starch-based crops are used commercially as biofuel feedstocks. The U.S. Department of Agriculture (USDA) and Oak Ridge National Laboratory have estimated that the United States could sustainably produce 1.3 billion metric tons of dry biomass/year using its agricultural (72% of total) and forest (28% of total) resources and still meet its food, feed, and export demands (Perlack et al. 2005). This amount of biomass has the energy content of 3.8 billion boe (barrels of oil energy equivalent) (Klass 1998). According to the U.S. Energy Information Administration, the United States consumes over 7.5 bbl/yr or billion barrels of oil per year (EIA 2008). According to the European Biomass Industry Association (EUBIA), Europe, Africa, and Latin America could produce biomass with an energy output of 1.4, 3.5, and 3.2 billion boe, respectively (e.g., see http://www.eubia.org/). The worldwide raw biomass energy potential in 2050 has been estimated to be 25 to 76 billion boe per year (IEA 2004). In addition to contributing to energy and chemical production, cultivation of biomass feedstocks can also have a positive effect on agriculture; for example, the USDA has estimated that the net farm income in the United States could increase from $3 to 6 billion annually if switchgrass became an energy crop (de la Torre Ugarte et al. 2003).

Governments around the world are promoting the biofuels industry by providing tax breaks, mandates, and agricultural subsidies, and devoting land to cultivation of biofuel feedstocks. The Chinese government is planning on devoting 50,000 square miles (approximately the size of Louisiana) for biofuels (Liu 2007). India has identified 154,000 squares miles (approximately the size of California) of marginal land for biofuel production.

New crops are being developed for biofuel and energy usage. Jatropha, which is a warm weather oilseed crop that requires a maturation period of 5 years, can be grown on marginal land. Figure 8.2 shows a jatropha plantation in India and the seeds. The oil yield for a mature jatropha plant is 5–13 boe/ha-yr (ha = hectare). Jatropha plantations are being planted in many countries in Asia, Africa, and Central and South America. Members of the Indian government hope that biodiesel produced from jatropha will replace 20% of the national's diesel fuel by 2012; the government is providing loans (total amount $34 million) to farmers to plant jatropha. Oil seeds are advantageous in that the technology for their conversion into biodiesel is inexpensive.

Figure 8.2. Jatropha plantation and oil seed (image sources from left to right: Jatropha World http://www.jatrophabiodiesel.org/; Government of Kanpur Dehat, India, http://kanpurdehat.nic.in/photograph.htm; Greenfueltech, http://www.greenfueltech.net/).

The yield of biomass from lignocellulosic energy crops can be up to 100 boe/ha-yr (Huber, Iborra, and Corma 2006). One example of a lignocellulosic energy crop that is being used in Europe is miscanthus, which is shown in Figure 8.3. Miscanthus has yield rates up to 75 boe/ha-yr and is a cold-tolerant perennial crop that requires very little fertilizer input. It is being grown commercially in Europe as a feed for electricity production in local area power stations. For miscanthus as for other biomass feed sources, the development of cost-effective and energy-efficient processes to transform the cellulose and lignin into fuels currently is hampered by a significant roadblock: a general lack of processes to deconstruct the biomass and transform the raw material into liquid fuels.

Figure 8.3. Miscanthus plantation and harvesting (image sources: [*left*] 1995 photo by Dr. I. Lewandowski, Institute for Crop Production and Grassland Research, University of Hohenheim, Germany, available at http://bioenergy.ornl.gov/papers/miscanthus/miscanthus.html; [*right*] University of Illinois at Urbana-Champaign, available at http://www.news.uiuc.edu/II/08/0207/index.html).

Liquid Fuels from Biomass

The main scientific challenge in converting biomass to a liquid fuel is how to efficiently remove oxygen from the biomass and produce a liquid product with good combustion and thermo-chemical properties (Huber, Iborra, and Corma 2006; Huber and Corma 2007). Oxygen can be removed as CO, CO_2 and H_2O. The general stoichiometry for biomass-conversion to liquid fuels (with glucose as the feedstock) is shown in Equation 8.1. All biomass conversion reactions follow this stoichiometry. A range of liquid biofuels can be produced, including alkanes, aromatics, and oxygenated fuels. To maximize the amount of energy in the liquid fuel, the oxygen should be removed as a combination of CO_2 and H_2O. The ratio of oxygen removed as CO_2 vs. H_2O depends on the products formed, as well as on whether or not hydrogen is used as a co-feed.

$$C_6H_{12}O_6 \rightarrow a\ C_xH_yO_z + b\ CO_2 + c\ CO + d\ H_2O \qquad (8.1)$$

There are currently many different approaches being used to convert biomass to biofuels. A summary of these approaches is shown in Figure 8.4, which shows routes that use chemical catalysts in black, routes that use biological routes in green, and routes that use either biological or chemical catalysts in blue. As shown in Figure 8.4, most of the routes to make biofuels use chemical catalysts. During the WTEC visits in Europe and Asia, panelists observed that all of the routes in Figure 8.4 are being studied and that the optimal route to make biofuels is currently not known. The technologies shown in Figure 8.4 are in different stages of development. It should be emphasized that considerable research and development is required to make liquid fuels economically viable. Petroleum-based liquid fuels are produced in high-volume, very efficient processes that have been continually optimized over the last 80 years.

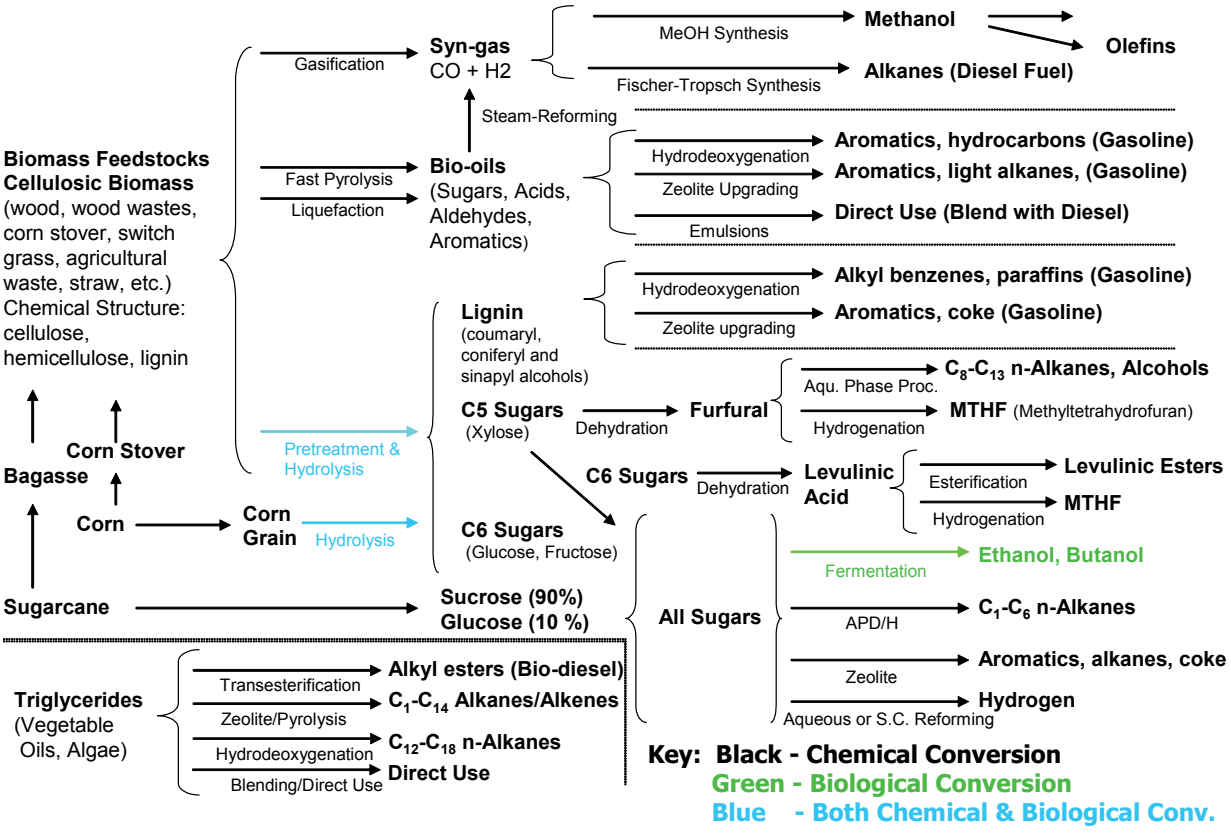

Figure 8.4. Routes for production of liquid fuels from biomass (adapted from Huber, Iborra, and Corma 2006).

Biomass Gasification and Syngas Conversion

Gasification of biomass and syngas conversion are probably the most technically developed areas of biofuel production. Several of the research groups the WTEC panel visited were studying biomass gasification, including Tsukuba University and Shell Global Solutions International. The panel also visited several groups that are studying syngas conversion, as described in Chapter 6.

There are several demonstration projects in Europe in which liquid fuels are being produced by Fischer-Tropsch synthesis (FTS) of lignocellulosic biomass. One is a joint demonstration plant of Shell and the Energy Research Centre of the Netherlands (ECN) that ran for 1000 hours, in which liquid biofuel was produced from wood by gasification and FTS (Boerrigter 2003; Boerrigter, den Uil, and Calis 2002). The researchers estimate the yield of diesel fuel from wood to be 120 L diesel fuel/metric ton biomass (Boerrigter 2003). Scandinavia-based Neste Oil Corporation and Stora Enso Group (a forest products company) have signed an agreement to develop liquid biofuels by FTS (Renewable Energy Access 2007). Their first step is to build an $18.7 million demonstration plant for this technology. Several companies in the United States are also involved in demonstrating this technology. Range Fuels (http://www.rangefuels.com), which will receive $76 million from the U.S. Department of Energy, is building a 20-million-gallon-per-year plant in Georgia. Range Fuels will convert the syngas into ethanol instead of alkanes.

The FTS route to fuel production from biomass requires several steps, including biomass gasification, tar removal, water-gas shift, and syngas conversion to fuels. Catalysis research is being done in all of these areas. Tar removal probably represents the currently most significant technical barrier that needs to be overcome for this process to become commercially viable.

Researchers in the Kunimori-Tomishige group at Tsukuba University are studying the production of syngas from biomass and how to reduce the tar formation in this process. They have shown (see Figure 8.5) that $Rh/CeO_2/SiO_2$ is particularly effective at converting biomass-derived tars into syngas (Asadullah et al. 2002).

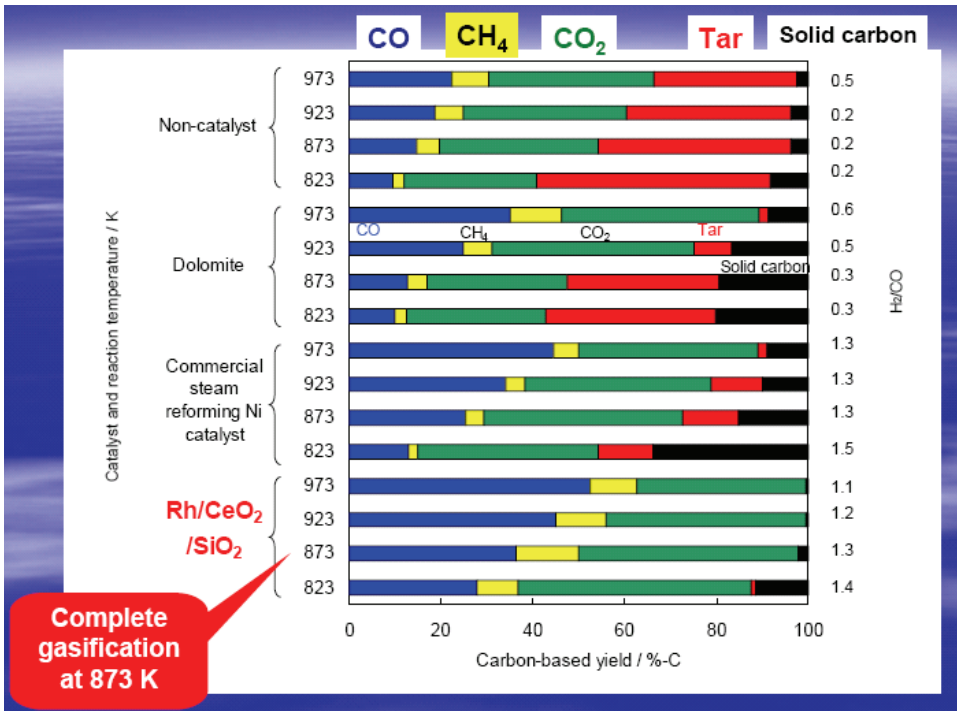

Figure 8.5. Catalytic gasification of biomass (cedar) with air (adapted from Asadullah et al. 2002). [Catalysts for biomass-reforming to syngas. This figure shows that $Rh/CeO_2/SiO_2$ is able to efficiently reform the tars (courtesy of Dr. Keiichi Tomishige).]

Several researchers in the United States, including the groups of Lanny Schmidt at the University of Minnesota (Salge et al. 2006) and Umit Ozkan at Ohio State, and researchers at the National Renewable Energy Laboratory (NREL) are also studying methods for catalytic gasification. Another growing area of interest is syngas conversion into ethanol. This is an area that is being studied at NREL and Pacific Northwest National Laboratory (PNNL), as well as by Jerry Spiney at Louisiana State University, Jim Goodwin at Clemson University, and Bob Davis at the University of Virginia.

Fast Pyrolysis and Bio-Oil Upgrading

Fast pyrolysis of biomass is a technology for production of a liquid fuel called bio-oil. Fast pyrolysis of biomass involves rapid heating (i.e., 500°C/s) of the biomass to intermediate temperatures (i.e., 500°C) without air, followed by rapid cooling. The liquid products produced by fast pyrolysis are a nonequilibrium mixture of more than 300 different bio-oil compounds. Fast pyrolysis of cellulosic biomass has been shown to produce bio-oils that contain up to 70% of the energy content of biomass feed (Huber, Iborra, and Corma 2006; Mohan, Pittman, and Steele 2006; Bridgwater and Peacocke 2000). Thus, fast pyrolysis is an efficient process for overcoming the recalcitrant nature of cellulosic biomass and producing liquid products.

The essential parameters for fast pyrolysis include the following (Bridgwater and Peacocke 2000):

1. A very high heating and heat transfer rate (i.e., 500°C/s).
2. Carefully controlled temperatures around 450–550°C
3. Rapid cooling of the pyrolysis vapors (residence time of less than 1 s).

One advantage of fast pyrolysis is that it can be done on a small scale (i.e., 50–100 tons biomass feed/day). This has led to the development of small-scale pyrolysis reactors like the one built on the back of a truck bed by Renewable Oil International, shown in Figure 8.6. Other promising technologies for biofuel production, such as cellulosic ethanol production or alkane production via gasification and Fischer-Tropsch Synthesis, are only economical at a large scale with feeds from 1000 to 8000 tons of biomass per day (Aden et al. 2002; Hamelinck and Faaij 2002; Hamelinck et al. 2004; Hamelinck, van Hooijdonk, and Faaij 2005; Prins, Ptasinski, and Janssen 2004). Many researchers worldwide are studying fast pyrolysis of biomass, as shown in Table 8.1. A review of fast pyrolysis reactors has been given by Bridgwater (1999). Of the 24 reactors listed in Table 8.1, only 6 of them are in the United States, demonstrating that the United States has not yet put significant resources into studying fast pyrolysis. Many of the pyrolysis reactors listed in the table are being operated commercially.

Figure 8.6. A small-scale portable reactor for liquid fuel production by distributed fast pyrolysis (courtesy of Renewable Oil International).

Table 8.1. Fast Pyrolysis Reactor Types and Locations Worldwide
(adapted from Mohan, Pittman, and Steele 2006)

Reactor Types	Locations
Ablative	Aston University (UK); NREL (U.S.); BBC (Canada); Castle Capital (Canada)
Auger	Renewable Oil International (U.S.); Mississippi State (U.S.); Advanced Biorefinery, Inc. (Canada)
Circulating fluidized bed	CPERI (Greece), CRES (Greece), ENEL (Italy)
Entrained flow	GTRI (U.S.), Egemin (Belgium)
Fluidized bed	Aston University (UK), Dynamotive (Canada); Hamburg University (Germany); Leeds University (UK); NREL (U.S.); Oldenburg University (Denmark); VTT (Finland)
Rotating cone	University of Twente (Netherlands); BTG/Schelde/Kara (Netherlands)
Transported bed	Ensyn (Canada and U.S.)
Vacuum moving bed	Laval University/Pyrovad (Canada)

One of the current challenges of fast pyrolysis is developing methods for conversion of bio-oils into liquid transportation fuels. Bio-oils cannot be used in conventional gasoline and diesel engines without upgrading. The bio-oils are chemically unstable and acidic (pH ~ 2.5). The acidity causes problems in diesel and gasoline engines. Pyrolysis-derived oils have a higher oxygen content, a higher moisture content, and a lower heating value (17 MJ/kg) than conventional fuel oil (43 MJ/kg). There are two methods that are being developed to improve bio-oils: (1) improve the fast pyrolysis process by catalyst addition; and (2) catalytic conversion of bio-oils into gasoline and diesel fuel.

KiOR (http://www.kior.com/, a privately funded joint venture) is developing a fast pyrolysis process that produces an improved bio-oil by the addition of catalysts to the process. In this process, catalytically accessible biomass is converted into a bio-crude suitable for further processing in new or existing oil refineries to gasoline and/or diesel fuel. Because of the enhanced accessibility of the biomass to the catalyst, the catalyst in BCC not only improves the secondary tar cracking, as in classical catalytic pyrolysis, but the catalyst also enhances the kinetics and selectivity of the primary conversion of the solid biomass. This allows for conversion at lower temperatures (improved energy efficiency), while producing improved-quality products. BCC can build on the long history of the technology of fluid catalytic cracking (FCC), the low cost workhorse of the oil refining industry.

Huber and coworkers at the University of Massachusetts-Amherst have shown that gasoline range aromatics can be produced from solid biomass-derived feedstocks when zeolite-based catalysts are introduced into the pyrolysis process (Carlson, Vispute, and Huber 2008). This process involves rapidly heating the biomass, where pyrolysis of the biomass to smaller organic fragments occurs (Figure 8.7). These molecules then enter the zeolite catalysts, where they are converted into aromatics, CO, water, and coke. The aromatic yield is highly dependent on both the active site and the pore structure of the catalyst.

One option for conversion of pyrolysis oils into liquid fuels is to use existing petroleum refinery technology, including hydrotreating and catalytic cracking (Huber and Corma 2007; Marinangeli et al. 2006). Some of the advantages of using existing infrastructure is that this results in lower capital costs. WTEC panelists who visited the Institute of Research on Catalysis and the Environment in Lyon, France (IRCELYON), heard about its project on hydrotreating and catalytic cracking of bio-oils, where its researchers are studying both model and real compounds. A recent review by Elliott (2007) discusses the historical developments of hydrotreating of bio-oils. At the time of this writing, bio-oils are not being used in a commercial-scale petroleum refinery. However, UOP (http://www.uop.com/) and Pacific Northwest National Laboratory (PNNL; http://www.pnl.gov/) have analyzed the opportunities of using bio-oils in existing petroleum refineries (Marinangeli et al. 2006). NESTE Oil and Shell are also studying how they could process bio-oils in petroleum refineries.

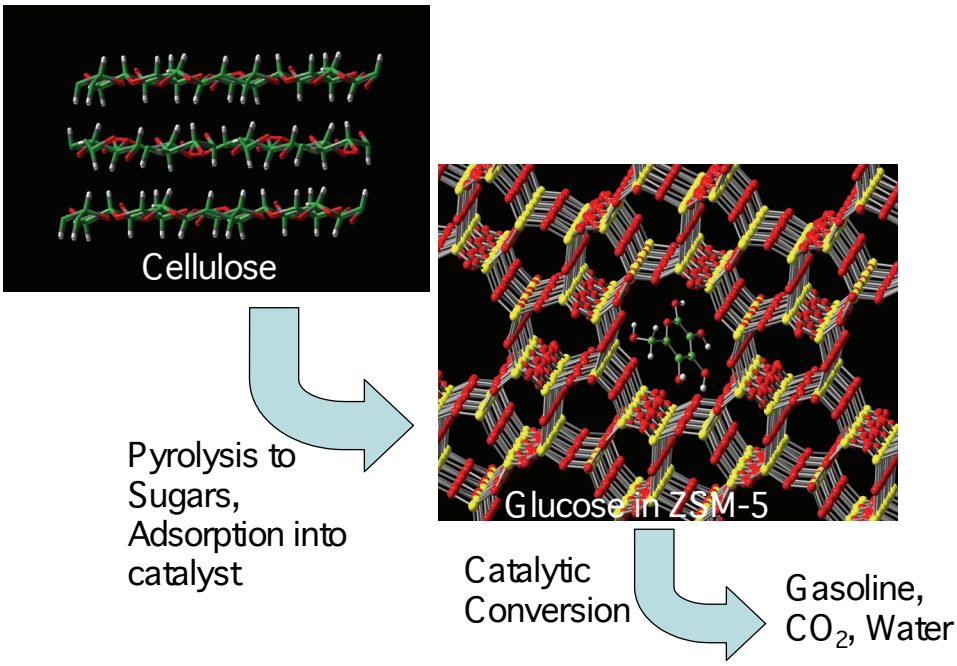

Figure 8.7. Green gasoline by catalytic fast pyrolysis of cellulosic biomass.

Liquid-Phase/Aqueous-Phase Catalytic Processing

The high functionality and low volatility of biomass make it particularly amenable to liquid-phase (or aqueous-phase) processing; this method is particularly advantageous because thermally unstable compounds can be converted selectively to liquid fuels. A wide variety of products can be formed by liquid phase processing, including liquid alkanes (diesel fuel replacement), light alkanes (gasoline range alkanes), gaseous alkanes (natural gas), and hydrogen (Huber and Corma 2007; Cortright, Davda, and Dumesic 2002; Huber et al. 2005; Huber and Dumesic 2006; Huber, Shabaker, and Dumesic 2003; Huber et al 2006). The overarching goal of liquid-phase catalytic processing of biomass-derived compounds (e.g., sugars) to produce liquid transportation fuels is to produce next-generation liquid fuels that (1) can be used with the existing infrastructure, (2) do not involve energetically intense distillation steps, and (3) have high rates of production per reactor volume. The next-generation liquid fuels produced by liquid-phase processing should have higher energy densities per volume (30–40 MJ/L) and have properties that are closer to those of gasoline and diesel fuel than ethanol (19 MJ/L).

High yields of well-defined liquid fuels are produced by liquid-phase catalytic processing. Liquid-phase catalytic processing of sugars is typically carried out at lower temperatures (e.g., 500 K) compared to biomass pyrolysis, liquefaction, or gasification. However, whereas these latter processes can operate with complex biomass feedstocks (e.g., containing cellulose, hemi-cellulose, and lignin components), liquid-phase catalytic processing typically involves feedstocks containing specific biomass-derived compounds such as sugars or polyols. Thus, another advantage of liquid-phase catalytic processing is that high selectivities and yields to targeted fuel compounds can be achieved, whereas a disadvantage of such processing is that real biomass feedstocks must be pretreated to prepare a feed solution that is appropriate for subsequent liquid-phase catalytic processing. Aqueous-phase processing work is being pioneered by James Dumesic at the University of Wisconsin (Cortright, Davda, and Dumesic 2002; Huber et al. 2005; Huber and Dumesic 2006; Huber, Shabaker, and Dumesic 2003; Chheda, Huber, and Dumesic 2007; Davda et al 2005; Huber, Cortright, and Dumesic 2004), and is being commercialized by Virent Energy Systems (http://www.virent.com/). A number of labs worldwide are starting to study aqueous-phase processing, including the University of Munich and Aristotle University of Thessaloniki (Greece) (Kechagiopoulos et al. 2006), and Fudan University (P.R. China) (Xie et al. 2006).

Vegetable Oil Conversion

The production of biodiesel by transesterification of vegetable oils is a technology that is experiencing almost exponential growth, as shown in Figure 8.8. Mineral bases are typically used as catalysts for the transesterification process (Huber, Iborra, and Corma 2006; Lopez et al. 2005; Lotero et al. 2005). These mineral bases introduce complex separation problems into the transesterification process. Heterogeneous catalysts are being developed to replace mineral bases in many labs worldwide. It has been projected that the development of a solid base catalyst for the transesterification step could reduce the cost of biodiesel by 30 cents per gallon (Goodwin et al. 2005). During their visits the WTEC panelists observed that there is a significant research effort in Europe on transesterification with solid base catalysts, including at IRCELYON and the Institut Charles Gerhardt Montpellier (ICGM) in France and at the Instituto de Tecnología Química (ITQ) in Spain. Most of the work at these institutions has not yet been published. In addition to the development of solid base catalysts for transesterification reactions, solid acid catalysts are also being developed for the esterification step in biodiesel synthesis (Lopez et al. 2005; Lotero et al. 2005; Mbaraka and Shanks 2005). This is an important step for biodiesel production if the vegetable oils contain large amounts of free fatty acids. Researchers in the United States are also developing solid catalysts for biodiesel production.

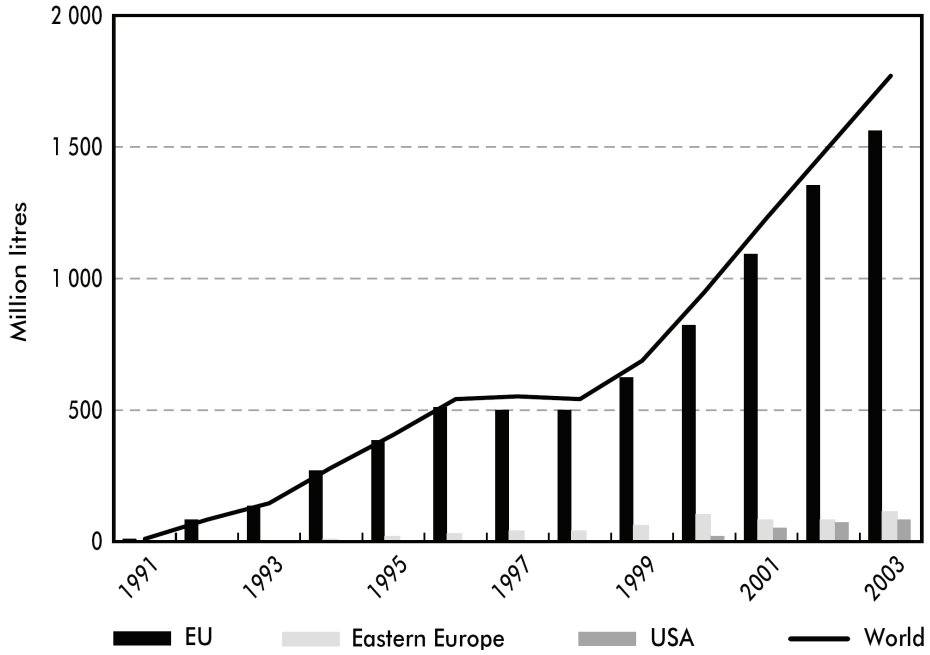

Figure 8.8. World and regional biodiesel capacity from 1991–2003 (IEA 2004).

Hydrotreating of vegetable oils to produce "green diesel" in existing petroleum refineries is another option for vegetable oil conversion that is moving to commercial scale (Huber and Corma 2007; Marinangeli et al. 2005; Huber, O'Connor, and Corma 2007). This technology is currently using standard hydrotreating catalysts that have been developed for petroleum oil feedstocks; in the future it is likely that new catalysts will be developed that are specifically made for vegetable oil feedstocks. Neste Oil has developed a NExBTL[6] renewable diesel production technology based on hydrotreating and is building two new units onto its Porvoo refinery in Finland, each of which has an annual capacity of 170,000 tons. Neste Oil will also be building a similar unit at Total's (http://www.total.com/) refinery in the UK. ConocoPhillips (http://www.conocophillips.com) has processed waste vegetable oil with petroleum oil in a unit of its Humber Refinery in the UK. ConocoPhillips would like to also use this technology in the United States;

[6] BTL = biomass to liquid

however, the U.S. government does not currently give the same subsidy for green diesel that it gives for biodiesel. UOP has also studied hydrotreating of vegetable oils in a petroleum refinery (Marinangeli et al. 2006). This author knows of no academic labs in the United States that are studying the hydrotreating of vegetable oils.

Chemicals from Biomass

Another area that is of growing importance is the production of chemicals from biomass. This area will become more important as more liquid fuels are produced from biomass, because byproducts from the fuel process can provide an inexpensive raw material that can be used to make chemicals. An example of this is the decreased cost and increased production of glycerol, which is a by-product of biodiesel refineries. Glycerol is being studied as a feedstock for production of a range of fuels and chemicals. A number of companies worldwide are starting to use bioplastics in their products. For example, Toyota uses polylactic acid in its Prius and Raum vehicles. Toyota is heavily investing in polylactic acid and hopes to control two-thirds of the polylactic acid market by 2020.

The conversion of biomass into chemicals involves the selective transformation of biomass-derived feedstocks. This involves a number of key fundamental reactions, including hydrogenation, dehydration, oxidation, hydrolysis, isomerization, and reforming (Chheda, Huber, and Dumesic 2007). These fundamental reactions can be combined with multifunctional catalysts where multiple reactions occur in a single reactor, such as in hydrogenolysis and dehydration/hydrogenation reactions.

The WTEC panel discussed the following biochemical projects with various hosts in Europe and Asia:

1. Hydrogenation and selective oxidation of sugars at IRCELYON. Similar research is also being done in the United States at the University of Virginia.
2. Furfural and 5-hydroxymethylfurfural (HMF) production by dehydration of sugars at Marseille. The group of Dumesic and researchers at PNNL are studying methods for furfural and HMF production (Chheda, Huber, and Dumesic 2007; Chheda, Roman-Leshkov, and Dumesic 2007; Roman-Leshkov, Chheda, and Dumesic 2006; Zhao et al. 2007) .
3. The production of sorbitol from cellulose (Hokkaido University Catalysis Research Center). Similar work is being done at University of Texas at San Antonio.
4. Production of 1,2 propanediol by hydrogenolysis of glycerol (University of Tsukuba). Members of the Kunimori-Tomishige group have studied the hydrogenolysis of glycerol to 1,2 propanediol and 1,3 propanediol. They have shown that this reaction occurs at lower temperatures with Ru/C + amberlyst (Miyazawa et al. 2006). They have also studied the reaction pathway (see Figure 8.9) and identified acetol as a key intermediate. They identified Rh/SiO_2 as a potential catalyst for 1, 3 propanediol production (Furikado et al. 2007). They are now starting to develop hydrogenolysis reactions for other biomass-derived oxygenated molecules. Similar work is also being done throughout the United States, including at Iowa State University, Michigan State University, the University of Missouri, and the University of Virginia.
5. Glycerol conversion by catalytic cracking (ITQ, Spain) (Huber and Corma 2007; Corma et al. 2007 and n.d.). Similar work is being done by Daniel Resasco at the University of Oklahoma.

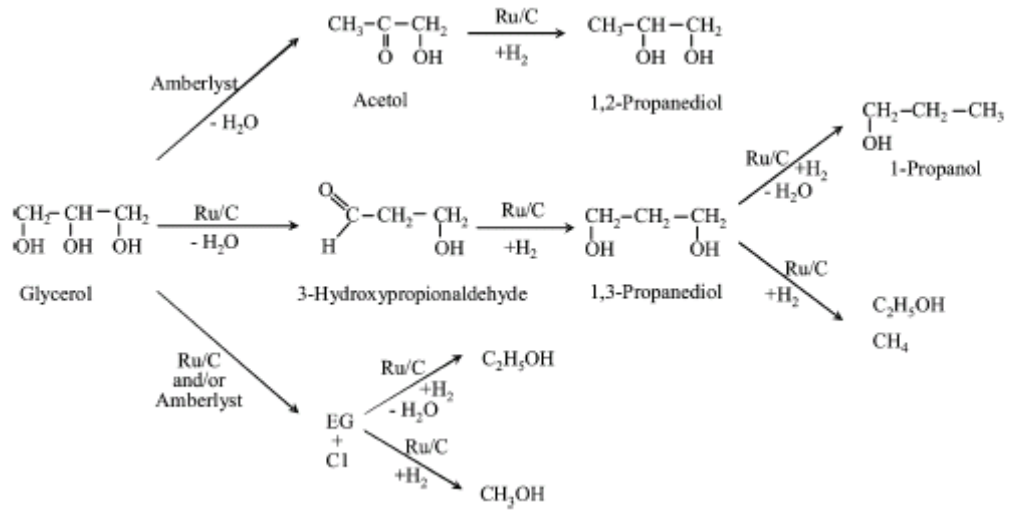

Figure 8.9. Reaction scheme for conversion of glycerol over Ru/C and amberlyst-based catalysts (from Miyazawa et al. 2006).

Bibliometric Analysis of Catalysis and Biofuels

WTEC commissioned a bibliometric analysis of catalysis papers that are related to biomass conversion. The full details of the bibliometric study are reported in Appendix D. As shown in Figure 8.10, from 1996–2005 only 1 out of every 400 catalysis papers was related to biomass conversion. However, in 2002 the number of papers published in this area started growing rapidly. Based on the results of the WTEC international assessment, it would seem that this area is continuing to grow worldwide.

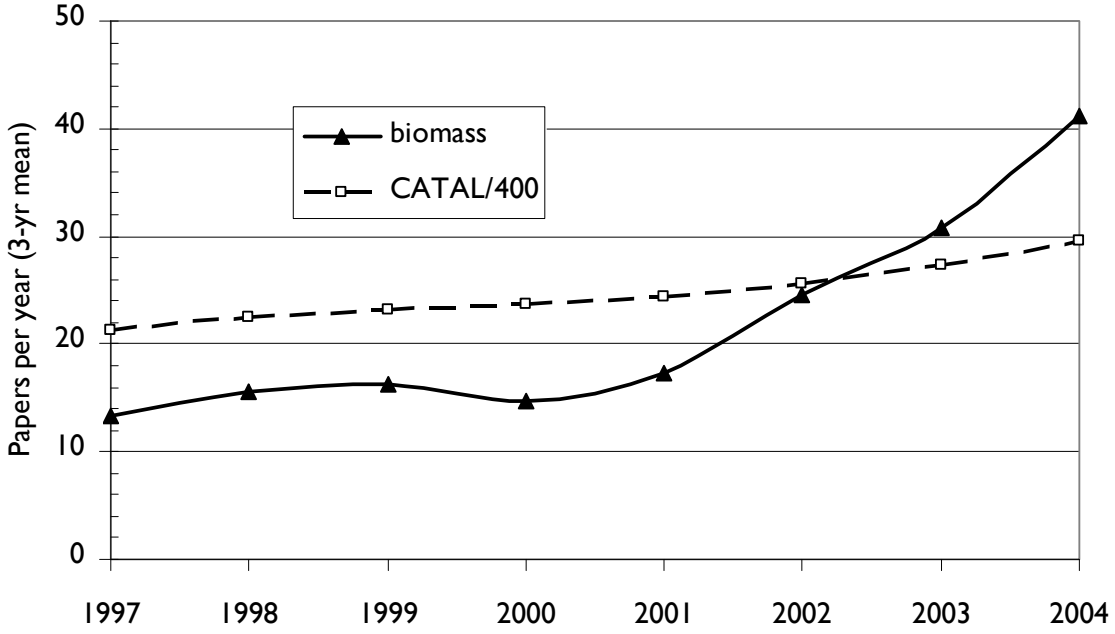

Figure 8.10. Catalysis papers (divided by 400) compared with catalysis papers relevant to biomass as a source of energy (biomass), 1996-2005, three-year running means (see also Appendix D).

The WTEC bibliometric study also indicated that less than 12% of the papers in catalysis related to biofuels came from the United States for the same time period, as shown in Figure 8.11. The majority of these papers came from the combined countries of Europe. This indicates that the United States is not putting as many resources into biofuel-related catalysis projects as Europe and Japan.

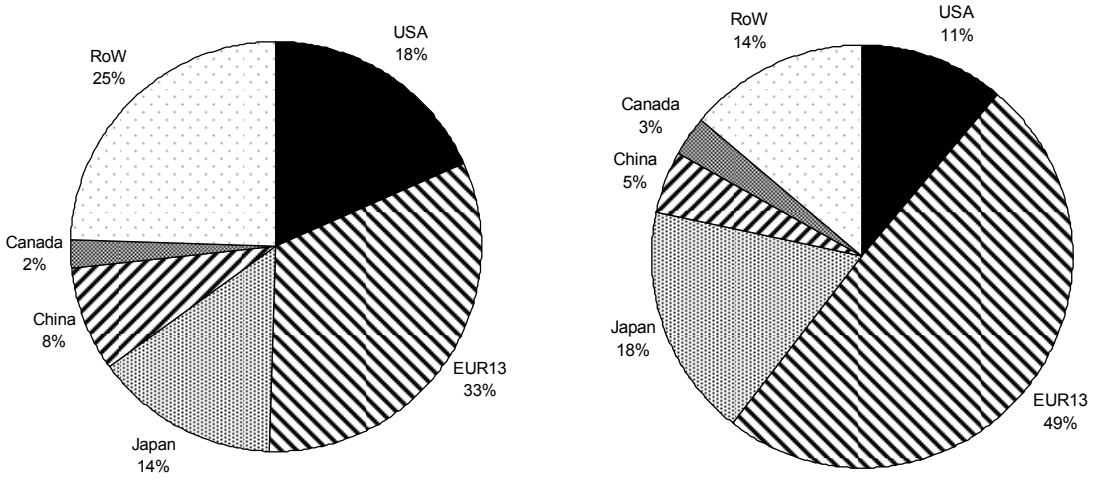

Figure 8.11. Geographical distribution of all catalysis papers (left) and catalysis papers related to biomass conversion (right), for the years 1996–2005 (see Appendix D for more details).

PHOTOCATALYTIC WATER SPLITTING

Another application of catalysis to renewable energy is the photocatalytic splitting of water with visible light to hydrogen and oxygen. This research work began with Honda and Fujishima in 1970, who demonstrated water splitting with a photoelectrochemical (PEC) cell (with a TiO_2 anode and Pt cathode) under UV irradiation and an external bias (Fujishima and Honda 1972). Several researchers that the WTEC panelists visited during the course of this WTEC study are working on photocatalytic splitting of water, including Domen (University of Tokyo); Fierro (Institute of Catalysis and Petrochemistry in Madrid); Hutchings (Cardiff University, UK); and several groups at the National Institute of Advanced Industrial Science and Technology (AIST) in Japan.

The basic principle of overall water splitting on a heterogeneous catalyst is shown in Figure 8.12. The overall water splitting is a large positive change in Gibbs free energy. Electrons in the valence band are excited into the conduction band by irradiation at an energy equivalent to or greater than the band gap of the photocatalyst, producing holes in the valence band. These electron-hole pairs cause reduction and oxidation reactions, respectively.

Domen and coworkers have developed a heterogeneous photocatalyst that can produce hydrogen from visible light in a single step, as shown in Figure 8.13 (Maeda and Domen 2007). The challenges associated with developing a suitable photocatalyst include finding materials that have the following properties: (1) band edge potentials suitable for overall water splitting; (2) band gap energy smaller than 3 eV; and (3) stability in the photocatalytic reaction.

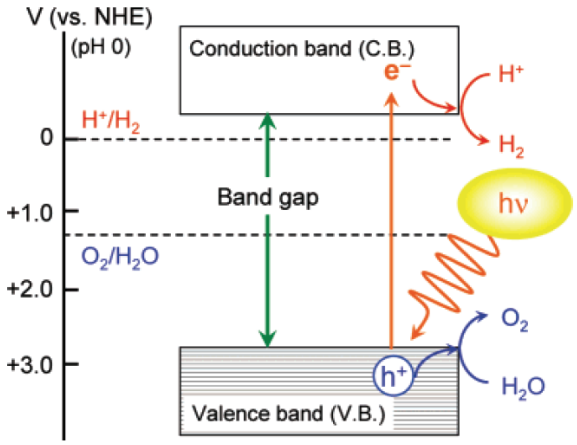

Figure 8.12. Basic principles of overall water splitting on a heterogeneous photocatalyst (from Maeda and Domen 2007).

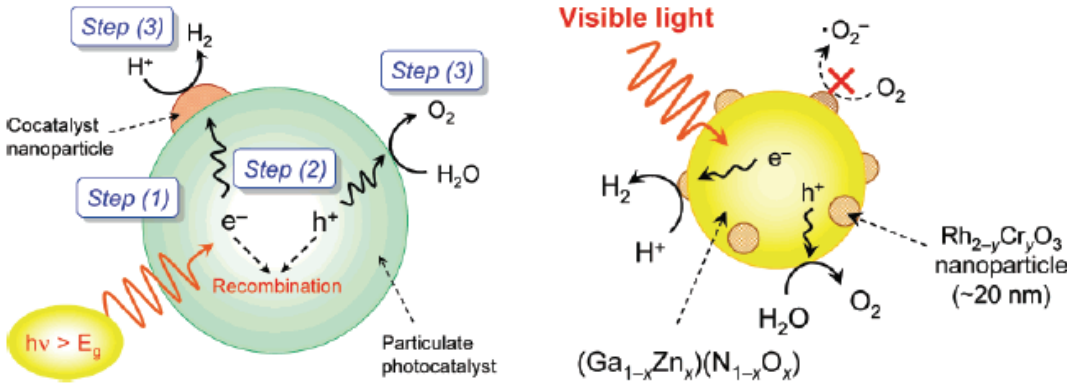

Figure 8.13. Heterogeneous photocatalyst for water splitting developed by Domen et al. (from Maeda and Domen 2007).

CONCLUSIONS

Using heterogeneous catalysis to convert renewable resources into liquid fuels, chemicals, and energy is currently a small field that appears to be growing exponentially. As fossil fuel prices continue to increase and as we look to solve problems caused by man-made CO_2 emissions, heterogeneous catalysis is likely to be part of the answer. There is a broad range of catalysis projects related to conversion of renewable resources, including different types of biomass and sunlight, into fuels and chemicals. It is likely that in the future catalysis will be used to convert our renewable resources into fuels and chemicals, just as today catalysis converts our nonrenewable resources into fuels and chemicals.

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APPENDIXES

APPENDIX A. PANELISTS' BIOGRAPHIES

Robert J. Davis, PhD, Panel Chair

PhD, Stanford University (Chemical Engineering, 1989)
MS, Stanford University (Chemical Engineering, 1987)
BS, Virginia Tech (Chemical Engineering, 1985)

Robert Davis has been professor and chair of Chemical Engineering (CHE Department) at the University of Virginia since 2002. After obtaining his PhD in 1989, he worked as a postdoctoral research fellow in the Chemistry Department at the University of Namur in Belgium. He joined the faculty in Chemical Engineering at the University of Virginia as an assistant professor in 1990, was promoted to associate professor in 1996, and to full professor in 2002.

Professor Davis has extensively used *in situ* spectroscopic methods coupled with both steady-state and transient kinetic methods to elucidate how oxide supports and basic promoters alter the active sites for a variety of catalytic reactions, including selective oxidation of hydrocarbons, acid/base reactions, and ammonia synthesis. Most recently, he has focused on the catalytic conversion of biorenewable carbon sources to fuels and chemicals. He and his group have illustrated how changes in the elemental composition, atomic structure, and reaction environment in the vicinity of a catalytic site influence both the activity and selectivity of chemical reactions.

He received the 2007 Paul H. Emmett Award in Fundamental Catalysis from the North American Catalysis Society, the NSF Young Investigator Award, the DuPont Young Professor Award, the Union Carbide Innovation Recognition Award, and the UVa Rodman Scholars Award for Excellence in Teaching. He has co-authored about 100 publications, 1 patent, and 1 textbook, *Fundamentals of Chemical Reaction Engineering*. He has delivered 100 invited lectures at conferences, academic departments, and industrial research groups, and has co-authored over 90 additional presentations at technical meetings.

Professor Davis has served as President of the Southeastern Catalysis Society, Chair of the 2006 Gordon Research Conference on Catalysis, Chair of Catalysis Programming of the AIChE, Director of the Catalysis and Reaction Engineering Division of the AIChE, Co-Chair of an International Catalysis Workshop in China, member of the Advisory Board of the International Conferences on Solid Acid and Base Catalysis, and member of the editorial boards of *Applied Catalysis A and B* and the *Journal of Molecular Catalysis A*.

Vadim V. Guliants, PhD

PhD, Princeton University (Chemistry, 1995)
MA, Princeton University (Chemistry, 1993)
Undergraduate, Moscow State University (Chemistry, 1987)

Vadim Guliants is professor in the Department of Chemical and Materials Engineering (CME) at the University of Cincinnati. He obtained his diploma in Chemistry (specializing in Physical Chemistry) with highest honors from Moscow State University (USSR) in 1987. Subsequently, he continued his studies in the Departments of Chemistry and Chemical Engineering at Princeton University. His PhD research centered on synthesis and characterization of novel vanadium-phosphorus-oxides for the partial oxidation of n-butane. Subsequent to receiving his PhD from Princeton, he joined R&D at Praxair, Inc., where his research focused on molecular modeling, synthesis, and characterization of microporous frameworks for gas separation. Vadim Guliants moved to the University of Cincinnati (UC) in 1999 as Assistant Professor of Chemical Engineering, where he was promoted to associate and full professor in 2003 and 2005, respectively. Professor Guliants also served as Associate Department Head of the Department of Chemical and Materials Engineering in 2004–2005.

Professor Guliants's research directions are in the areas of (1) mixed metal Mo-V-based oxides for partial (amm)oxidation of lower alkanes, (2) novel nanostructured Ni based catalysts for partial oxidation and reforming of renewable and fossil feedstocks, and (3) nanostructured biocatalytic membranes employing entrapped lipases and monoxygenases for chemical processing and other applications. The unifying theme of his research is elucidating the fundamental relationships between the molecular structure of these materials and their function for the purpose of rational design of new improved functional materials for applications spanning chemical and environmental catalysis and separations.

He has received the NSF CAREER Award, NSF NIRT Award, University of Cincinnati College of Engineering Outstanding Research Award for Young Faculty, University of Cincinnati Teaching Diversity Award, and a Soros Scholarship at Oxford University. He has co-authored about 80 publications and 6 patents. He has delivered over 50 invited lectures at conferences, academic departments, and industrial research groups, and has co-authored over 90 additional presentations at technical meetings.

Professor Guliants has served as Director of the TriState (OH, KY, WV) Catalysis Society, Chair of Ceramic Materials Programming of the AIChE, Secretary of the ACS Catalysis Secretariate, and a guest editor of several issues of *Catalysis Today* and *Topics in Catalysis*.

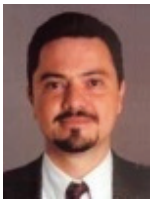
George W. Huber, PhD

PhD, University of Wisconsin, Madison (Chemical Engineering, 2005)
MS, Brigham Young University (2000)
BS, Brigham Young University (1999)

George Huber is an assistant professor (and Armstrong Professor) of Chemical Engineering at the University of Massachusetts-Amherst. His research focus is on breaking the chemical and engineering barriers to

lignocellulosic biofuels. Prior to his appointment at UMass, Dr. Huber did a post-doctoral stay with Avelino Corma at the Technical Chemical Institute at the Polytechnical University of Valencia, Spain (UPV-CSIC), where he studied biofuels production using petroleum-refining technologies. While obtaining his PhD in Chemical Engineering from University of Wisconsin-Madison, he helped develop novel aqueous-phase catalytic processes for biofuels production under the guidance of Jim Dumesic. At Brigham Young University where he obtained his BS and MS degrees and studied Fischer-Tropsch Synthesis, Calvin H. Bartholomew was his MS advisor.

Dr. Huber has authored 25 peer-reviewed publications, including two papers in *Science* and three articles in *Angewandte Chemie International Edition*. He has five patents in the area of biofuels. His research is being commercialized by two different companies (Virent Energy Systems and Bio-e-con). He is currently working with governmental and industrial institutions to help make cellulosic biofuels a reality. He is the chair for an NSF/DOE workshop entitled, "Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels" (http://www.ecs.umass.edu/biofuels).



Raul F. Lobo, PhD

PhD, California Institute of Technology (Chemical Engineering, 1995)
MSc, California Institute of Technology (Chemical Engineering, 1993)
Licenciatura, University of Costa Rica (Chemical Engineering, 1989)

Raul Lobo is full professor in the Department of Chemical Engineering and is Associate Director of the Center for Catalytic Science and Technology at the University of Delaware. His research interests span the development of novel porous materials for catalysis and separations, the characterization of disordered zeolite structures, and the scientific aspects of catalysts synthesis. After receiving his PhD in the study of new molecular sieves and zeolites from CalTech, he worked for one year at Los Alamos National Laboratory, New Mexico, as a postdoctoral fellow. He started his academic career at the Center for Catalytic Science and Technology, University of Delaware, in the fall of 1995.

Professor Lobo has published over seventy refereed reports and he is co-inventor in three U.S. patents. He has been recipient of the NSF CAREER award, the Camille Dreyfus Teacher-Scholar award, the Young Scholar Award of the Francis Alison Society, the Outstanding Young Faculty Award of the College of Engineering (University of Delaware), the Innovation Recognition Program Award of the Dow Chemical Company, and the Ipatieff Prize of the American Chemical Society.

Professor Lobo has been member of the Structure Commission of the International Zeolite Association since 1999, and he is member of editorial board of *TIP Revista Especializada en Ciencias Químico-Biológicas, México*. He has been a visiting fellow at the Centre for High-Resolution Electron Microscopy at Delft University of Technology in The Netherlands. In 1997 he was a member of the executive committee of the International Zeolite Conference, and in 2003 he organized the Symposium Transmission Electron Microscopy and Catalysis and was chair of the Catalysis and Reaction Engineering Division of AIChE.

Jeffrey T. Miller, PhD

PhD, Oregon State University (Chemistry, 1980)
MS, University of New Mexico (Inorganic Chemistry, 1973)
BS, Memphis State University (Chemistry, 1971)

Jeff Miller is Senior Scientist in the heterogeneous catalysis group at the Argonne National Laboratory, developing testing and characterization of new catalytic materials for energy production. His focus is on characterization of catalysts under realistic reaction conditions of high temperature and pressure, especially via use of EXAFS spectroscopy at the Advanced Photon Source. He is also an adjunct professor in the Department of Chemical Engineering and a member of the College of Engineering Advisory Board of the University of Illinois at Chicago; in addition, he has been a mentor at Northwestern and Purdue universities.

Prior to the summer of 2008, Dr. Miller was Senior Research Scientist at BP Chemical Company. After earning his PhD in 1980 he joined the exploratory catalyst and process development group of Amoco Oil Company (now BP) in Naperville, IL. His work at BP Chemical Company was focused on developing new catalytic materials for new chemical plants. His research interests at BP included synthesis, characterization, and applications of zeolite and nanoparticle heterogeneous catalysts, especially the use of *in situ* X-ray absorption spectroscopy for elucidation of the role of the support, size, and composition on the changes in structure and electronic properties of metal nanoparticles, and how these alter performance.

Dr. Miller received the 2006 Herman Pines Award for outstanding research in the field of catalysis from the Chicago Section of the North American Catalysis Society, for which he has also served as area director. Through collaborations with several leading academic groups in the United States and Europe, Dr. Miller has co-authored over 100 publications and been granted 45 U.S. patents. Additionally, he has been on the editorial board of *Applied Catalysis A: General* and has been on the organizational committees for several international meetings.

Matthew Neurock, PhD

PhD, University of Delaware (Chemical Engineering, 1992)
BS, Michigan State University (Chemical Engineering, 1986)

Matt Neurock is Alice M. and Guy A. Wilson Professor of Chemical Engineering and professor of Chemistry at the University of Virginia. From 1992–93, he was a postdoctoral fellow at the Eindhoven University of Technology in The Netherlands. He returned to the United States in 1993 to work for the DuPont Chemical Company as a visiting scientist in its Corporate Catalysis Center. He joined the faculty of Chemical Engineering at the University of Virginia in 1995 as an assistant professor and was promoted to full professor in Chemical Engineering and in Chemistry in 2003. His research interests include computational heterogeneous catalysis, molecular reaction engineering of complex systems, surface bonding, and reactivity. He has developed and applied *ab initio* as well as stochastic methods to simulate the kinetic behavior of complex catalytic systems, including electrocatalysis, oxygenate synthesis, alkane activation, exhaust emissions, solid acid catalysis, the conversion of biorenewables, and catalyst deactivation.

Professor Neurock received the 2005 Paul H. Emmett Award in Fundamental Catalysis from the North American Catalysis Society. He was named the Johansen-Crosby Lecturer by Michigan State University in 2006, Distinguished Catalysis Researcher by Pacific Northwest Laboratory in 2004, and Visiting Professor by the University of Montpellier in 2007. He has also been the recipient of an NSF Career Development Award, a DuPont Young Faculty Award, and a Ford Young Faculty Award. He has co-authored over 145 publications, two patents, and two books. His most recent book, published in March 2006, is titled, *Molecular Heterogeneous Catalysis: A Conceptual and Computational Approach*. He was recently appointed as an editor for the *Journal of Catalysis*.

Renu Sharma, PhD

PhD, University of Stockholm (Solid State Chemistry, 1985)
MS, University of Stockholm (Solid State Chemistry, 1984)
BS and BEd in Physics and Chemistry, Panjab University, India (1970)

Renu Sharma is Director of the Industrial Associates Program and Research Scientist at the LeRoy Eyring Center for Solid State Science at Arizona State University (ASU). Subsequent to receiving her PhD in Sweden in 1985, she came to ASU as a faculty research associate. She was appointed as assistant research scientist in the Center for Solid State Science in 1989, was promoted to associate research scientist with tenure in 1995, and to senior research scientist in 2008. In 1992 she joined as affiliated faculty the Science and Engineering of Materials program, which is now the School of Materials. Her research is primarily focused on atomic-scale *in situ* observations of the nanoscale synthesis processes and effects of ambient conditions on the functioning of nanomaterials, such as catalyst nanoparticles, carbon nanotubes, and silicon nanowires. This is achieved using an environmental scanning transmission electron microscope (ESTEM), established under her leadership, that combines atomic-level observations with chemical analysis of reaction processes. She has successfully developed and employed this unique technique to obtain atomic-level mechanisms involving the reactivity of nanoparticles, including surfaces, defects, commensurate and non-commensurate structures in nonstoichiometric inorganic solids, and ceramics.

Dr. Sharma has received fellowships from Swedish Institute (1980), University of Stockholm (1981), and Deutscher Akademischer Austauschdienst (DAAD) (2000). Her students have won best poster awards and travel grants from AIMS, MSA, and NAM in 1991, 2006 and 2007, respectively. She has edited one book and has published one book chapter and 60 articles. She has presented over 40 invited papers at various institutes and conferences and has co-authored over seventy presentations at various national and international conferences.

She is past president of the Arizona Imaging and Microanalysis Society. She has also organized a symposium at Materials Research Society (MRS) and chaired sessions at Microscopy Society of America and MRS meetings. She has participated in three workshops, organized by DOE (2001), NSF (2006) and NIST (2006), and has chaired one NSF-sponsored workshop (2006), all in the general areas of *in situ* electron microscopy and nanotechnology. She has served as guest editor of *Microscopy and Microanalysis*.

Levi T. Thompson, PhD

PhD, University of Michigan (Chemical Engineering, 1986)
MSE degrees, Chemical Engineering and Nuclear Engineering, University of Michigan (1983)
BChE, University of Delaware (Chemical Engineering, 1982)

Levi Thompson is Richard E. Balzhiser Collegiate Professor of Chemical Engineering, Professor of Mechanical Engineering, and Director of the Center for Catalysis and Surface Science at the University of Michigan, Ann Arbor. He is also Director of the Michigan-Louis Stokes Alliance for Minority Participation, a $5 million, NSF-funded program that teams the University of Michigan, Western Michigan University, Michigan State University, and Wayne State University in an effort to significantly increase the number of minority students earning science, technology, engineering, and mathematics baccalaureate degrees. After earning his PhD and working for two years at KMS Fusion, Inc., he joined the faculty of the U. Michigan Department of Chemical Engineering in 1988 and was promoted to full professor in 2000. From 2001 to 2005, Professor Thompson served as Associate Dean for Undergraduate Education, in which capacity he led the College of Engineering's student recruitment and support efforts to promote excellence and diversity in the undergraduate student body.

Research in Professor Thompson's group at the University of Michigan focuses primarily on the design and development of high-performance catalytic, electrocatalytic, and adsorbent materials, and on defining relationships between the structure, composition, and function of nanostructured catalytic and electrocatalytic materials. In addition, his group works on the use of micromachining and self-assembly methods to fabricate hydrogen production systems and fuel cells. Professor Thompson's publications include an invited contribution on batteries for the *World Book Encyclopedia* and review articles on carbide and nitride catalysts, and hydrogen production. He has been awarded 10 patents. In 2007, he was appointed founding director of the Hydrogen Energy Technology Laboratory, a unit of the Michigan Memorial Phoenix Energy Institute. This laboratory was established to support multidisciplinary hydrogen production, storage, and conversion research, and is housed in the Phoenix Memorial Laboratory.

Professor Thompson's honors and awards include the NSF Presidential Young Investigator Award, Engineering Society of Detroit Gold Award, Union Carbide Innovation Recognition Award, Dow Chemical Good Teaching Award, College of Engineering Service Excellence Award, and Harold Johnson Diversity Award. He is cofounder, with his wife Maria, of T/J Technologies, a developer of nanomaterials for advanced batteries, and in 2006 he founded Inmatech, Co., Ltd., to commercialize catalytic materials and processes discovered and developed in his U. Michigan laboratories. Professor Thompson is Consulting Editor for the *AIChE Journal*, and he is a member of the External Advisory Committee for the Center of Advanced Materials for Purification of Water with Systems (NSF Science and Technology Center at the University of Illinois), the National Academy's Committee on the Assembled Chemical Weapons Alternatives Programs, the AIChE Chemical Engineering Technology Operating Council, and the National Academy's Chemical Sciences Roundtable.

APPENDIX B. BIBLIOMETRIC ANALYSIS OF CATALYSIS RESEARCH, 1996–2005

Grant Lewison, Evaluametrics Ltd, Richmond, Surrey, TW9 4JF, England

SUMMARY

This study examined the outputs of catalysis research recorded in the Science Citation Index. The USA was the largest producer, but its quantitative dominance of catalysis was much less than in many other scientific fields, and Western Europe published almost twice as much. The output of the People's Republic of China is expanding rapidly and is now greater than that of Japan. The potential citation impact of U.S. papers was the highest in the world, although that of some European countries, notably Switzerland, was almost as high. By contrast, East Asian papers tended to appear in low-impact journals. An analysis was also made of the small number of papers in biomass research involving catalysis. Leading catalysis research institutions in Europe and East Asia were identified as an aide to the panel's selection of sites to visit.

INTRODUCTION

There were two main objectives of this study: to compare U.S. research outputs in the field of catalysis with those of other leading countries, both quantitatively and in terms of likely impact; and to help the panel identify appropriate laboratories for their visits and leading researchers within them.

Bibliometrics is the quantitative study of publications, more specifically of research papers in the serial literature, usually restricted to articles and reviews. It has been practiced for more than 80 years, but it was given great impetus in the early 1960s with the creation by Eugene Garfield of the Science Citation Index (SCI) and more recently by the advent of powerful computers that can analyze the bibliographic details of large numbers of papers. Because bibliometric analysis is a purely mechanical process, whereby individual scientific papers are categorized in various ways, it should not be seen as the only approach to research evaluation. Rather, it is a complement to peer review, and its conclusions need to be validated by those with experience of the subject under study. Nevertheless, its objectivity can often be advantageous, as it is hard for even dispassionate observers to be able to sum up the achievements of a whole country, and to put them in context.

This study examined world outputs in a single field, and so the first step was to define this field and then create a "filter" that would selectively identify relevant papers within a bibliographic database and allow their details to be downloaded to a spreadsheet. From the addresses on the papers, a geographical analysis could be conducted, with the outputs of different countries, and of cities and institutions within them, determined. There is an assumption often made in bibliometrics to the effect that the impact of a paper on other researchers will be correlated with the frequency with which papers in the same journal are cited by other papers. This is not true at the individual paper level, but the correlation between potential and actual citation impact is surprisingly high for large groups of papers, such as those from a particular country. Bibliometric analysis is quite good at ranking countries and institutions working within a field on the basis of the journals in which they are published. This represents the considered opinions of an editorial board and several referees who will have read the paper carefully before accepting it for publication. However it is clearly not the same as the direct effect of the paper on other researchers, whose citation of it is sometimes treated as the only useful measure of research quality.

METHODOLOGY

As mentioned above, the first step in the analysis was to define the subject area, or field, for investigation. The definition was written by Professor Bob Davis, the panel chairman, and agreed with other panelists. It reads as follows:

> Heterogeneous catalysis involves the selective acceleration of a chemical reaction on an active site located on the surface of a solid material. Although catalysis involves molecular change, the nanostructure surrounding the active site is critical for activity and selectivity of the catalyst. The influence of nanostructure on catalysis includes but is not limited to the following: modification of the electronic structure by a quantum size effect, molecular traffic control and shape selectivity in nanometer-sized pores, optimal interactions of promoters and supports with active sites, cooperativity of active sites in multifunctional catalysts, and the liquid structure of the reaction medium that can provide alternate paths for catalytic reactions.

Based on this definition, a filter was created in close consultation with Prof Davis that consisted of five parts:

A. Names of specialist catalysis journals

B. Title words that alone indicated that the paper was relevant to catalysis

C. Title words indicative of "activity"

D. Title words indicative of an element or other structure used for catalysis

E. Title words showing that the paper was not, in fact, relevant to catalysis as defined

Papers were selected for analysis if they met criteria A or B, or C + D, but did not contain E. Tables B.1 to B.5 show the journals and title words in the five lists, A to E. In Tables B.2–B.5, an asterisk denotes any character(s), or none.

Table B.1. Set A: Specialist Catalysis Journals

Advanced Catalysis	*Journal of Catalysis*
Applied Catalysis A General	*Journal of Molecular Catalysis A Chemical*
Applied Catalysis B Environmental	*Journal of Molecular Catalysis B Enzymatic*
Catalysis Reviews Science & Engineering	*Kinetic Catalysis (English Translation)*
Catalysis Surveys from Asia	*Microporous & Mesoporous Materials*
Catalysis Today	*Reaction Kinetics & Catalysis Letters*
Catalysis Letters	*Studies in Surface Science & Catalysis*

Table B.2. Set B: Title Words Alone Indicative of Catalysis

Ag/Al_2O_3	Cocataly*	Pd/SiO_2
Au/ Al_2O_3	$CoMo/ Al_2O_3$	Photocataly*
Au/Fe_2O_3	Electrocataly*	Photoelectrocataly*
Au/SiO_2	Enzym* + Immobiliz*	Precatalyst*
Au/TiO_2	Fe*ZSm*	Pt/Al_2O_3*
Autocatal*	Nanocataly*	Pt/ZrO_2*
Biocatal*	Ni/ Al_2O_3	Ru/Al_2O_3
Catalys*	Organocataly*	Sn/ Al_2O_3
Catalyt*	Pd/ Al_2O_3	Sonocatalysis

Table B.3. Set C: Title Words Indicative of Catalytic Activity

Activat*	Desorption	Hydroformylat*	Oxidat*
Activit*	Desulfurizat*	Hydrogenat*	Oxygen Storage
Adsorb	DFT	Hydroisomerizat*	Photooxidat*
Adsorbate	Epoxidat*	Hydrolysis	Preparation
Adsorbates	Esterificat*	Hydroprocess*	Reaction*
Adsorbed	Friedel	Hydrotreat*	Reactivit*
Adsorbing	Growth	Hydroxylat*	Reduction*
Adsorbs	HDS	Immobiliz*	Reforming
Adsorption	Heck	Isomerizat*	Selectivit*
Adsorption/Desorption	Hydrocrack*	Kinetic*	Suzuki
Aromatizat*	Hydrodechlorinat*	Metathesis	Transesterificat*
Deactivat*	Hydrodemetalliz*	Methylat*	Trimerizat*
Dehydrat*	Hydrodenitrogenat*	Oligomerizat*	Tropsch
Dehydrogenat*			

Table B. 4. Set D: Title Words Indicative of an Element or Structure Used for Catalysis

Ag	Graphite	Molybdenum*	Re/*	Tin
Ag/*	$H_3PW_{12}O_40$*	Molybdophos*	Rhenium*	Tin/*
Au	$H_3PMo_{12}O_40$	Montmorillonite*	Rh	TiO_2*
Au/*	Heterogenous	Mordenite*	Rh/*	Titania
Carbide*	Heteropoly	Nanocluster*	Rhodium*	Titanium
Ce	Heteropolyacid*	Nanocrystalline	Ru	Tungsten
Ce/*	Hydrotalcite*	Nanoparticle*	Ru/*	Tungstophosphoric
CeO_2	Ir	Ni	Ruthenium*	V
Ceria	Ir/*	Ni/*	Salen	V/*
Cerium	Iridium*	Nickel*	Sapo	V_20_5
Chromium*	Keggin	$NiMo/Al_2O_3$	SBA	Vanadia
Cluster*	La	Nitride*	Schiff	Vanadium*
Cobalt	La/*	Oxide*	Sieve*	Vanadyl
Co/*	Lanthanum	Palladium*	Silicalite	W
Copper	Manganese*	Pd	Sn	W/*
Cr	MCM	Pd/*	Sn/*	Zeolite*
Cr/*	Mesoporous	Perovskites	Sulfide*	Zirconia
Cu	Microporous	Pillared	Ta	Zirconium*
Cu/*	Mn	Platinum*	Ta/*	Zr
Fe	Mn/*	Polyoxometalate*	Tantalum	ZSM
Fe/*	Mo	Pt/*	Ti	
Gold*	Mo/*	Re	Ti/*	

Table B.5. Set E: Title Words to Exclude Non-Catalysis Papers

DNA*	Protein*	Protease*	RNA*	Solar Cell*

The filter was calibrated with reference to papers with and without address terms such as catalysis and its equivalents in some other European languages [although the titles of all papers are translated in the SCI into English, with US spelling, the words in the addresses are often left in the original language, transliterated as necessary into the Roman alphabet]. Its precision was determined as 0.62 and its recall as 0.78. These are not particularly high values (values > 0.9 are not uncommon in biomedical subject areas), but then catalysis is a relatively diffuse subject. This means that the apparent world output of catalysis papers should be multiplied by 0.62 / 0.78 = 0.795 to obtain an estimate of the correct number of papers.

During the study, attention was focused on the use of catalysis to promote the industrial exploitation of biomass for energy purposes, and it was decided to carry out a subanalysis of papers that appeared to be relevant to this subject area. They were selected by means of title words selected by one of the panelists, Professor George Huber, and were as listed in Table B.6.

Table B.6. Title Words Used to Characterize Catalysis Papers as Being Relevant to Biomass as a Source of Renewable Energy

Bagasse	Biodiesel	Biofuel OR Bio-Fuel
Biomass NOT (Detox OR Sorption OR Removal)		
Biooil OR Bio-Oil	Sugarcane OR Sugar-Cane	
Glycerol AND (Hydrogenolysis OR Oxidation)	Sugar AND (Hydrolysis OR Oxidation)	

The addresses on the papers were analyzed by means of a special macro (written by Dr. Philip Roe) that determined for each paper the fractional count of each country listed in the addresses, and also the integer count. A paper with two addresses in the USA, one in France, and one in Germany would count 0.5 for the USA and 0.25 each for France and Germany on a fractional count basis; it would count unity for each country on an integer count basis. Fractional counts enable the totals for groupings of countries, such as the European Union or Latin America, to be determined; they are also more representative of a country's true contribution to the field.

On the other hand, integer counts enable a country's relative commitment (RC) to catalysis research to be compared with its presence in all science. This ratio shows the relative importance of catalysis research for the country, with the value for the world being unity. It has the advantage that it compensates, to some degree, for biases in the SCI for or against some countries because of language or other reasons, on the assumption that catalysis research papers are as likely as ones in other fields of science to be published in journals processed for the SCI.

The **potential citation impact** (PCI) of each of the papers in the file was determined on the assumption that they would be cited as frequently as other papers in the same journal. The citation time window was five years, i.e., the year of publication and four subsequent years. Data on the mean citation rates of papers in each journal were obtained from Thomson Scientific (the publishers of the SCI) for every other year in the period 1996-2002: they do not normally change much in a two-year period. The mean PCI for leading countries was then calculated for three cohorts of papers: 1996-99, 2000-02 and 2003-05. Some values of PCI for leading journals used by catalysis researchers in the four periods are shown in Table B.7.

Table B.7. Leading Journals Used by Catalysis Researchers, their Percentage Usage in 2003–05, and their Potential Citation Impact Factors in 1996–97, 1998–99, 2000–01, and 2002+.

Journal	%	1996-	1998-	2000-	2002+
Angewandte Chemie-International Edition	1.28	20.3	21.2	23.2	29.3
Journal of the American Chemical Society	2.77	22.9	23.1	25.7	28.5
Applied Catalysis B-Environmental	1.59	12.4	14.5	16.7	20.2
Chemistry-a European Journal	0.62	18.3	18.3	18.3	17.2
Journal of Catalysis	2.71	12.9	12.2	14.1	16.0
Applied Catalysis A-General	4.05	8.2	7.4	9.4	14.9
Journal of Molecular Catalysis A-Chemical	3.93	6.4	7.3	6.4	10.2
Catalysis Letters	1.84	8.9	7.6	7.3	7.5
Reaction Kinetics and Catalysis Letters	0.99	1.8	1.9	2.1	2.4
Studies in Surface Science and Catalysis	2.82	3.5	2.3	2.3	1.9
Kinetics and Catalysis	0.72	0.6	0.7	0.7	1.1

To meet the second objective of the study, namely to assist the panel in the identification of the leading institutions carrying out catalysis research in Europe and East Asia, it was necessary to perform an analysis of the institutional addresses for selected countries (three in East Asia and 13 in Europe). This is the first item in the address, and appears in contracted form, e.g., Chinese-Acad-Sci, Jilin-Univ, Natl-Inst-Mat-Sci. Sometimes different forms are used for institution names, and unification is needed in order to determine the true total for an institution. For the purposes of this study, a count was made of the numbers of addresses appearing during the last three years, viz., 2003-05; this will usually be slightly more than the numbers of papers, but the ranking of institutions is unlikely to be much affected. Some national scientific institutions (e.g., Chinese-Acad-Sci, CNRS in France, CSIC in Spain, CNR in Italy) have many locations, and for these, the leading cities also needed to be determined so that their outputs could be compared with those of single-centre institutions such as universities.

RESULTS: QUANTITATIVE OUTPUTS

Figure B.1 shows the growth of catalysis research outputs compared with all science, as recorded in the SCI. (Allowance has been made for the shortfall of papers in 2005 because of late recording.) The former is growing at about 5.4% per year, compared with just 2.9% per year for all science, so it can be regarded as a rapidly-growing field. Figure B.2 shows the outputs of the leading countries, presented as three-year moving averages so as to smooth out annual variations, on a fractional count basis. “Europe 13” sums the output of the countries listed in Table B.8.

Table B.8. 13 European Countries Used for Institution Location Analysis

Country	Code	Country	Code	Country	Code	Country	Code
Austria	AT	France	FR	Netherlands	NL	Sweden	SE
Belgium	BE	Germany	DE	Norway	NO	Switzerland	CH
Denmark	DK	Italy	IT	Spain	ES	UK	UK
Finland	FI						

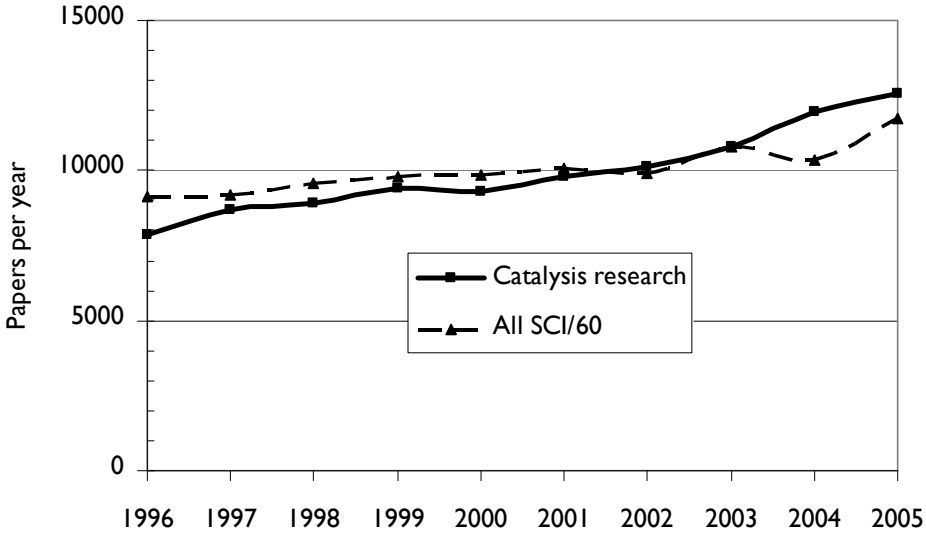


Figure B.1. World outputs of catalysis research papers (after application of calibration factor), solid line, and of all science (divided by 60), dashed line, 1996-2005.

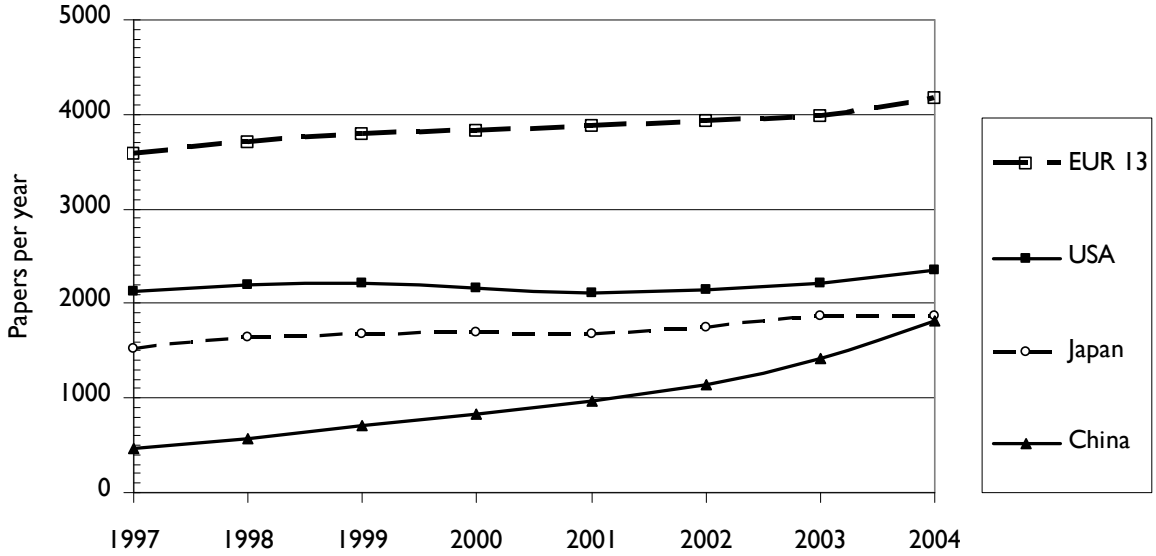


Figure B.2. Outputs of catalysis research papers (not corrected for CF) from 13 European countries, the USA, Japan and China (People's Republic), 1996-2005, three-year averages.

China's output has been growing rapidly, and in 2005 it was greater than that of Japan. The output of the 13 European countries listed in Table B.6 is collectively almost twice that of the United States; in most other fields of science, the outputs of Western Europe and the United States are similar in magnitude. The outputs of the leading European countries are shown in Figure B.3 on a different scale to that of Figure B.2.

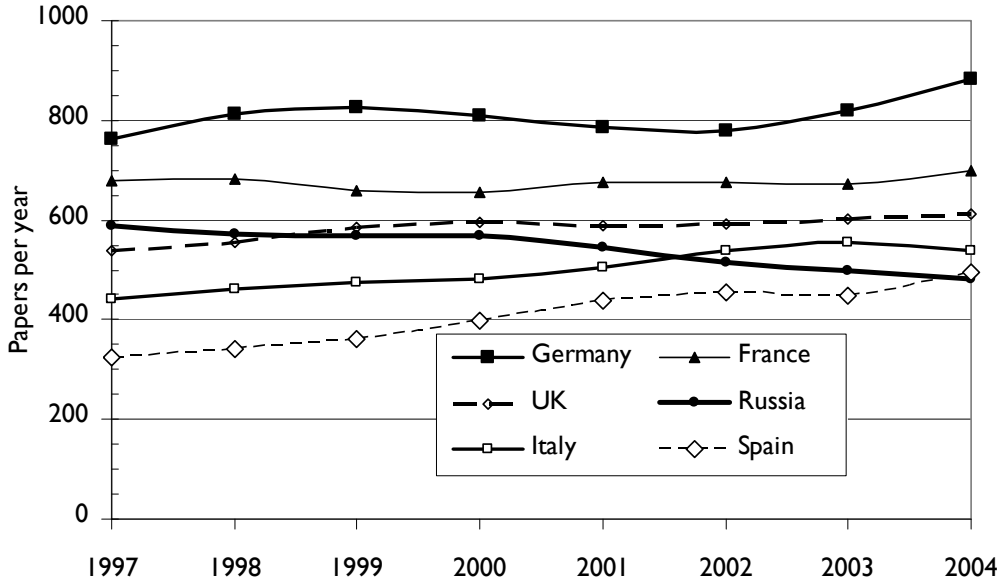


Figure B.3. Catalysis research outputs (uncorrected) for six European countries, 1996–2005, three-year moving averages.

Whereas the outputs of Germany, France, and the UK have been rather stable (although that of Germany is now increasing), and those of Italy and Spain have been increasing; that of Russia has been declining, and it is now the lowest of the six.

The outputs of some East Asian countries are shown in Figure B.4: those of China and Japan have been divided by two so as to make them more on a scale with those of the others. This makes it very clear that Japan, China, and the Republic of Korea are the main producers of catalysis research, and that the other so-called "tigers", Taiwan and Singapore, are minor players in this activity.

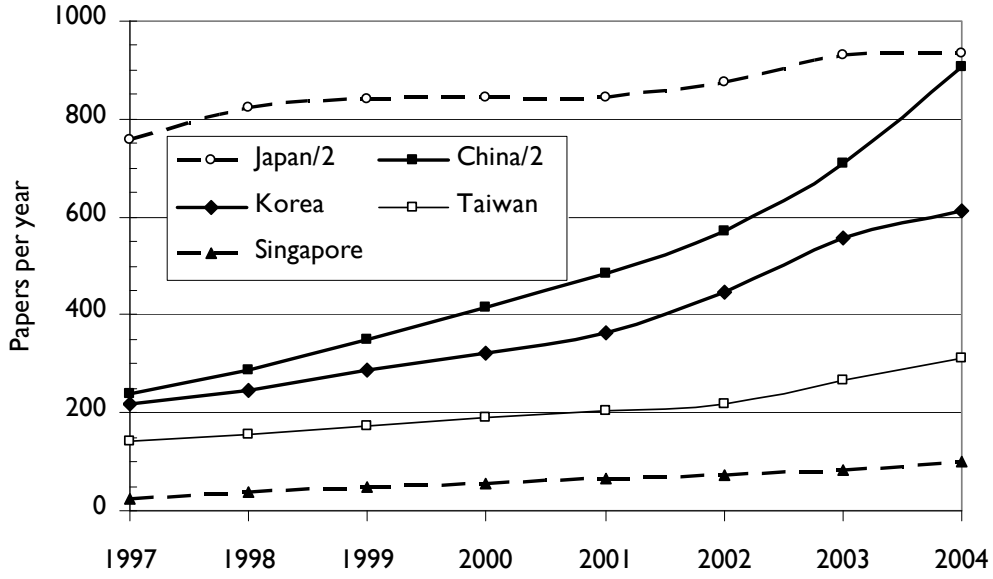


Figure B.4. Catalysis research outputs (uncorrected) for five East Asian countries, 1996-2005, three-year moving averages.

The relative commitments to catalysis research, compared with all science, are shown in Figure B.5. This makes it clear that China is making a big commitment to the field, as are the other East Asian countries shown, but that the field is of relatively low priority in the United States and Canada, and also in the UK, perhaps reflecting a low interest in chemistry and the chemical industry in these countries.

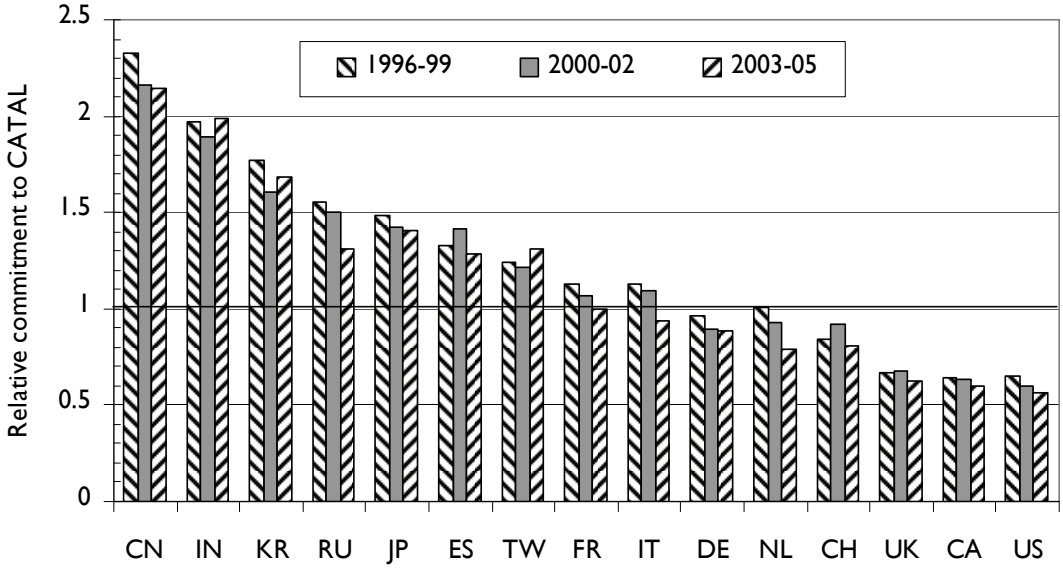


Figure B.5. Relative commitments of leading countries to catalysis research, 1996-2005.
CN = China ,IN = India, KR = Korea, RU = Russia, JP = Japan, TW = Taiwan, CA = Canada.

The mean potential citation impact (PCI) of the journals used by different countries to publish their catalysis papers is shown in Figure B.6. (The mean values for the whole world in the three periods were 8.4, 9.1, and 9.0 cites in five years.) Clearly on this criterion, the United States is still the leading country, although Switzerland (CH) appears to be catching up quite rapidly. The East Asian countries are still publishing in below-average impact factor journals, although Japan's output is not far below the world average.

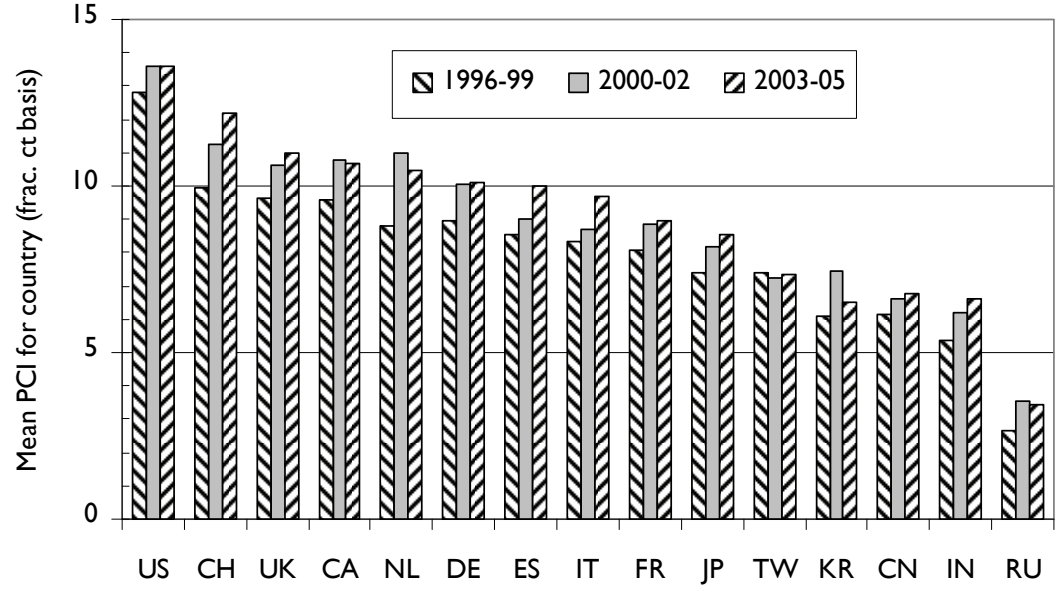


Figure B.6. Mean Potential Citation Impact factor of journals used to publish catalysis research papers by leading countries, 1996–2005 (fractional count basis).

The overall impact of catalysis research can be calculated as the product of the mean PCI and the number of papers. On this indicator, and using fractional counts, Table B.9 shows the relative performance of North America (the USA + Canada), Europe 13 (with the contributions of the six leading countries specified), and East Asia (five countries). The table also shows the ratio of the overall impact of Europe 13 and East Asia to North America in the three periods.

Table B.9. Overall Potential Citation Impact (PCI x number of papers) of Catalysis Research from Different Countries and World Regions in 3 Periods

Region/Country	1996–1999	2000–2002	2003–2005
North America	120525	91001	95128
US	110464	82608	86164
CA	10060	8393	8965
Europe 13	126505	108063	111777
DE	27619	22476	23637
UK	20973	18030	17240
FR	21468	17158	16628
IT	14919	12689	14513
ES	11263	11498	13504
NL	8546	7270	6524
Others	21718	18942	19731
East Asia 5	68507	68715	90624
JP	45281	39143	41916
CN	12251	16235	29869
KR	5585	7887	10559
TW	4376	4071	6098
SG	1014	1380	2183
Ratio, Eur13/NA	1.05	1.19	1.18
Ratio, EA/NA	0.57	0.76	0.95

It appears that Europe is increasing its dominance over that of North America, and that East Asia is catching up quickly and may have equaled the total impact of North America in 2007.

The output of catalysis papers relevant to biomass as a source of energy was small, only 233 in the 10-year period used for analysis, but it grew rapidly after 2001, as shown in Figure B.7.

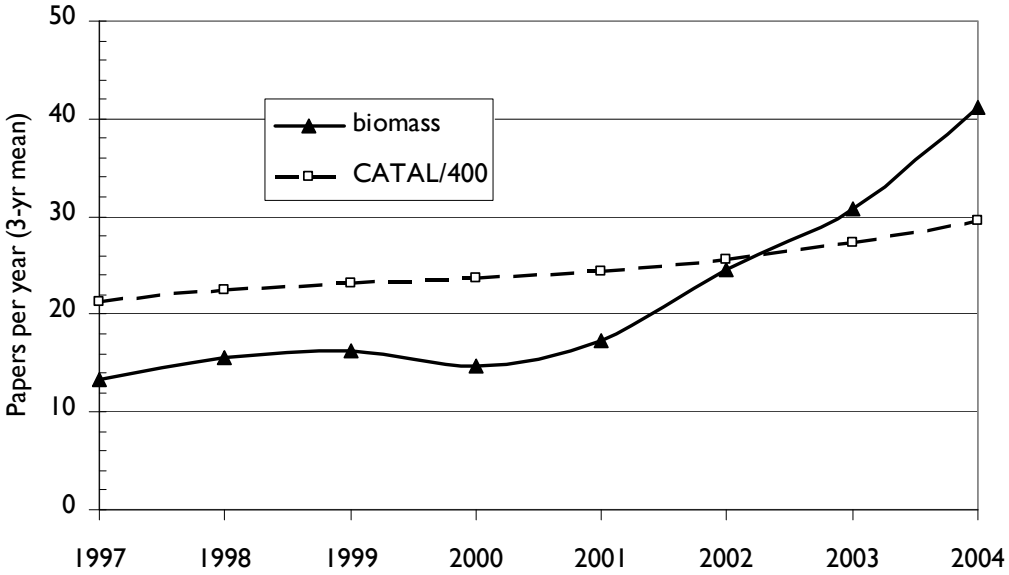


Figure B.7. Output of catalysis papers (corrected for calibration factor and divided by 400) compared with that of papers relevant to biomass as a source of energy, 1996-2005, three-year running means.

Compared with all catalysis research, the USA published relatively less, and the 13 European countries relatively more, see Figure B.8.

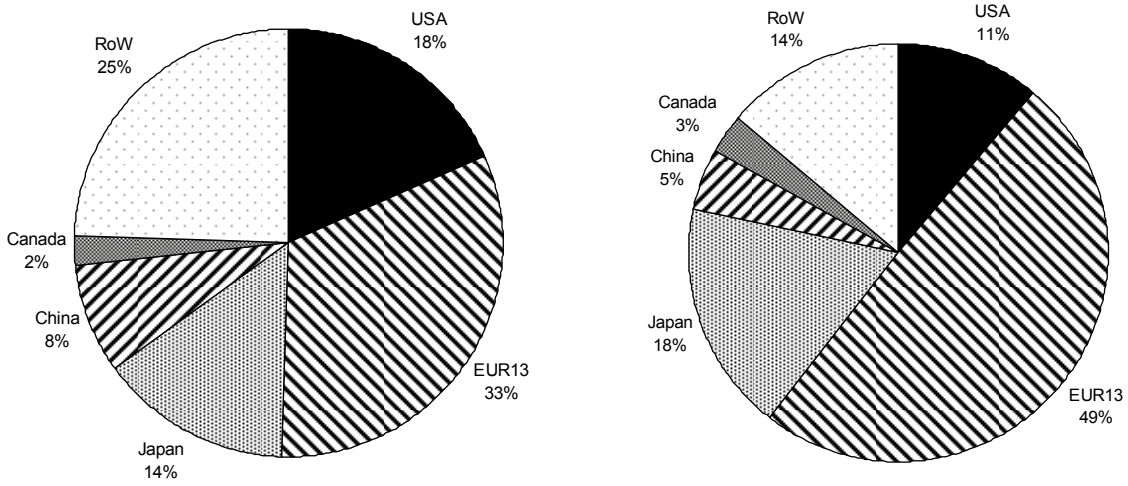


Figure B.8. Geographical distribution of catalysis papers (left) and biomass ones (right).

However the United States published its relatively few biomass papers in high-impact journals, and in ones of higher PCI than those it used for catalysis papers overall, whereas the reverse was the case for all other countries; see Figure B.9.

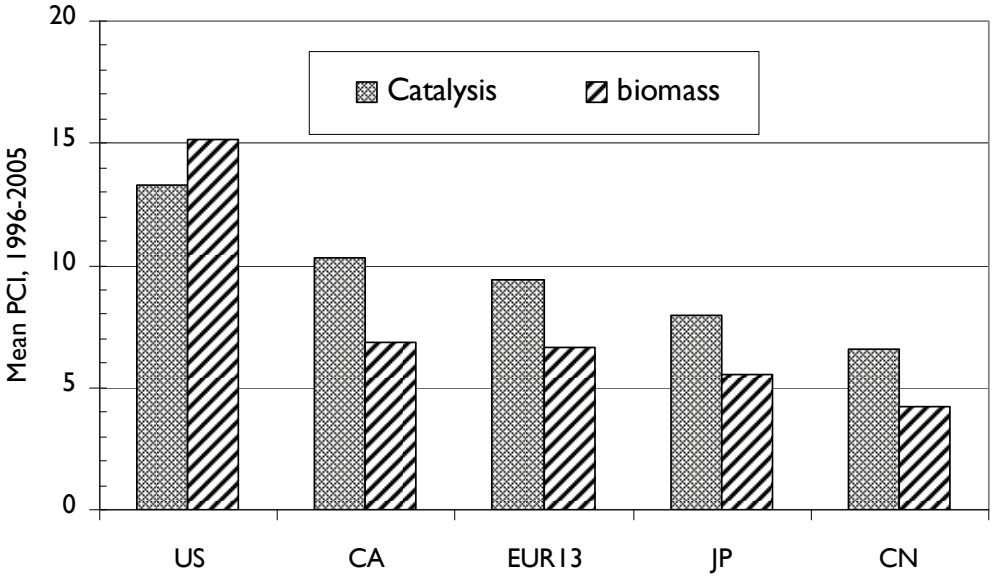


Figure B.9. Mean five-year potential citation impact factors for biomass papers from different geographical areas, compared with those for all catalysis papers, 1996–2005

RESULTS: LEADING INSTITUTIONS IN CATALYSIS RESEARCH

Table B.10 shows the leading institutions in catalysis research in the three leading East Asian countries, and Table B.11 shows the corresponding data for the 13 European countries listed in Table B.8.

CONCLUSIONS AND DISCUSSION

Catalysis, as defined by the evaluation panel, is a small but growing area of research. The United States publishes relatively little (compared with its dominance of science in most other fields) but its papers are of high potential citation impact. These remarks apply with particular strength to catalysis papers concerned with biomass for energy, where U.S. output is only 11% of the world but the papers are in very high impact journals. European overall catalysis output is now almost twice that of the USA and some countries, notably Switzerland, are approaching it in terms of potential citation impact. In East Asia, China has now overtaken Japan in terms of output (this occurred in 2005), and Korea's publications are also increasing rapidly, though their potential citation impact is still quite low.

Some limitations of bibliometric analysis need to be pointed out. There are inevitable biases in the journal coverage of the SCI; in particular of journals not in English, which are bound to have a more limited readership. One effect of this is to *improve* the average PCI of papers from countries whose output has been affected, as the papers in purely national journals, with low citation counts, have not been taken into consideration. However it is likely that the best labs in these countries will publish the large majority of their papers in international journals.

Another limitation is that counts of papers in the SCI may not reflect the amount of research activity in commercial companies, where considerations of confidentiality will inevitably limit the amount that they seek to publish. This is likely to be of more importance in a field such as chemistry than in biomedicine, where publication of clinical trial results is a pre-requisite to the licensing of a new drug, and publication of new research achievements is the way to advancement for young biotech companies. Thus Shell in Amsterdam, a major company in catalysis, only published 11 papers in 2003–05.

Table B.10. Leading Catalysis Research Institutions in China, Japan, and Korea, 2003–05 (numbers of addresses on catalysis papers)

Country	Institution	N
JP	Univ. Tokyo, Meguro Ku, Tokyo 1538904	996
JP	Tohoku Univ, Sendai, Miyagi 9808578	831
JP	Kyoto Univ, Kyoto 6068501	800
JP	Tokyo Inst Technol, Yokohama, Kanagawa 226850	795
JP	Osaka Univ, Suita, Osaka 5650871	764
CN	Chinese Acad Sci, Beijing 100080	748
JP	Hokkaido Univ, Sapporo, Hokkaido 001002	685
JP	Natl Inst Adv Ind Sci & Technol, Tsukuba, 3058565, or Osaka 5638577	622
KR	Seoul Natl Univ, Seoul 151742	622
CN	Chinese Acad Sci, Shanghai 200032	544
CN	Dalian Inst Chem Phys, Dalian 116023	542
CN	Fudan Univ, Shanghai 200433	526
CN	Zhejiang Univ, Hangzhou 310032	510
CN	Tsing Hua Univ, Beijing 100084	484
JP	Kyushu Univ, Kasuga, Fukuoka 8168580	463
CN	Nanjing Univ, Nanjing 210093	454
CN	Jilin Univ, Changchun 130023	443
JP	Nagoya Univ, Nagoya, Aichi 4648603	435
KR	Korea Adv Inst Sci & Technol, Taejon 305701	389
CN	Univ. Sci & Technol China, Hefei 230026, Anhui	387
CN	Xiamen Univ, Xiamen 361005	297
KR	Pohang Univ. Sci & Technol, Pohang 790784	282
CN	Nankai Univ, Tianjin 300071	275
CN	Chinese Acad Sci, Lanzhou 730000	272
JP	Sci Univ. Tokyo, Shinjuku Ku, Tokyo 1628601	248
CN	Tianjin Univ, Tianjin 300072	237
KR	Hanyang Univ, Seoul 133791	236
CN	Hong Kong Polytech Univ, Kowloon, Hong Kong	235

Table B.11. Leading Catalysis Research Institutions in 13 Leading European Countries, 2003–05
(numbers of addresses on catalysis papers). For country codes, see Table B.8.
Note: the last three institutions are ones visited by the panel, but they are not the next three in rank order. Not all 13 countries have an institution with 230 or more addresses in 2003-05.

Country	Institution	N
ES	CSIC, 28040 Madrid	710
NL	Delft-Univ-Technol	450
IT	Univ-Milan	436
FR	Univ-Paris-06, 75252 Paris 05	416
UK	Univ-Cambridge	405
FR	Inst-Rech-Catalyse, 69626 Villeurbanne	380
CH	ETH-Honggerberg, 8093 Zurich	370
DE	Tech-Univ-Munich, 85747 Garching	363
IT	Univ-Turin	332
NL	Univ-Utrecht	301
NL	Eindhoven-Univ-Technol	300
DE	Max-Planck-Gesell, Fritz Haber Inst, 14195 Berlin	297
FR	Univ-Lyon-1, 69626 Villeurbanne	290
ES	Univ-Barcelona, 08028 Barcelona	284
UK	Univ-London-Imperial-Coll	283
CH	Ecole-Polytech-Fed-Lausanne, 1015 Lausanne	280
UK	Univ-Liverpool	278
IT	Univ-Roma-La-Sapienza	276
SE	Chalmers-Univ-Technol, 41296 Gothenburg	271
BE	Univ-Catholique-Louvain, 1348 Louvain	267
ES	CSIC, UPV, Inst Tecnol Quim, 46022 Valencia	264
IT	Univ-Padua	259
FR	Univ-Strasbourg-1, 67070 Strasbourg	243
UK	Univ-Oxford	236
DE	Max-Planck-Inst-Kohlenforsch, 45470 Műlheim	233
UK	Cardiff-Univ	207
DK	Tech-Univ-Denmark, 2800 Lyngby	172
DK	Haldor-Topsøe-Res-Labs, 2800 Lyngby	109

No attempt has been made to determine the actual citation impact of papers from different countries as a check on the values of potential impact based on journals. This was primarily because the number of papers was so large (more than 125,000 over the decade) that even a sample of several thousand might have been quite unrepresentative. Citation counts are but one measure of "quality". The links between universities and industry may be a more meaningful indicator of the relevance of the research being carried out in academia. These could be co-authorships, but other, less visible links such as research sponsorship, paid consultancies and industrial placement of students, could also be indicative of industrial relevance.

APPENDIX C. SITE REPORTS—ASIA

Site: **AIST (National Institute of Advanced Industrial Science and Technology)**
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Ibaraki, 305-8565 Japan
http://www.aist.go.jp/index_en.html

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BACKGROUND

The National Institute of Advanced Industrial Science and Technology (AIST) is the largest public research organization in Japan. The WTEC team visited the headquarters of AIST in Tsukuba. There are 10 other AIST research labs distributed throughout Japan. AIST has four central missions (see http://www.aist.go.jp/index_en.html):

1. Sustainable society. AIST seeks to provide a high-quality, safe, and sound life where people and nature co-exist.
2. Increase Japanese industrial competitiveness. AIST helps to strengthen the industrial competitiveness through innovations in industrial technology by being an innovation hub.

3. Increase local development of industrial policies. AIST helps local industrial technology by strengthening cooperation among local industries, academia, and governments.
4. Contribute to industrial technology policies. AIST helps the Japanese government by analyzing information on industrial science and technology and supporting policymaking on strategies.

AIST tries to bring together academia and industry, to be an innovation hub and integrate human resources, systems, and organizations. In developing new technologies, AIST takes a long-term approach, focusing on developing fundamental basic science for applied research problems. AIST has defined two different types of research phases: Type 1 research whose purpose is to discover and elucidate new scientific knowledge, and Type 2 research, which is focused on integration and application. Type 1 research is generally associated with generating new ideas and new processes. In contrast, Type 2 research takes these ideas and turns them into a practical reality. Figure C.1 shows the vision of AIST in taking a scientific idea and turning it into reality. The first 0–5 years consists of Type 1 research that has to do with discovery or invention. Type 2 research occurs during the following 5–15 years in which the basic research is transformed into an industrial product. AIST staff calls this phase the "nightmare" technology phase.

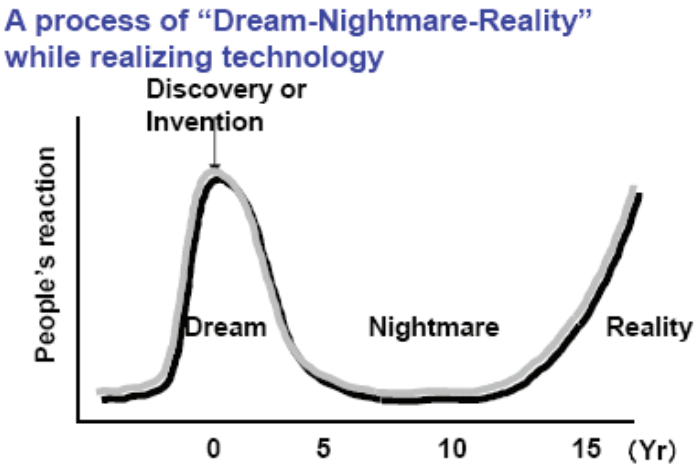

Figure C.1. AIST vision of turning basic science into an economic reality (originally proposed by Josef Hatvany and Hiroyuki Yoshikawa in 1983; courtesy of AIST).

Previously AIST was part of Ministry of International Trade and Industry (MITI). However, in 2001, MITI was reorganized and AIST became a separate entity. The FY2006 budget for AIST is $810 million (¥98,547 million). It can be broken down into the following: 67% subsidy from government; 23% commissioned research funds (or competitive national grants); 6% facilities and management grants; and 4% from industry and royalties. AIST has 3191 employees, of which 2025 are tenured researchers, 462 are fixed-term researchers, and 704 are administrative staff.

AIST consists of 28 research centers, 21 research institutes, and 7 research initiatives. The research centers conduct pioneering and strategic projects in a 7-year period. They are operated in a top-down management model where upper management sets the research priorities. The research institutes have longer-term research goals. Research themes are proposed in a bottom-up manner by the researchers themselves. The research initiatives are designed to promote the formation of new research fields and/or research centers.

There are six research themes at AIST:

1. Life Science & Technology
2. Information Technology & Electronics
3. Nanotechnology, Materials, & Manufacturing

4. Environment & Energy
5. Geological Survey & Applied Geoscience
6. Metrology & Measurement Technology

The composition of the research staff at AIST is shown in Figure C.2, which indicates the degree of emphasis in the six research areas.

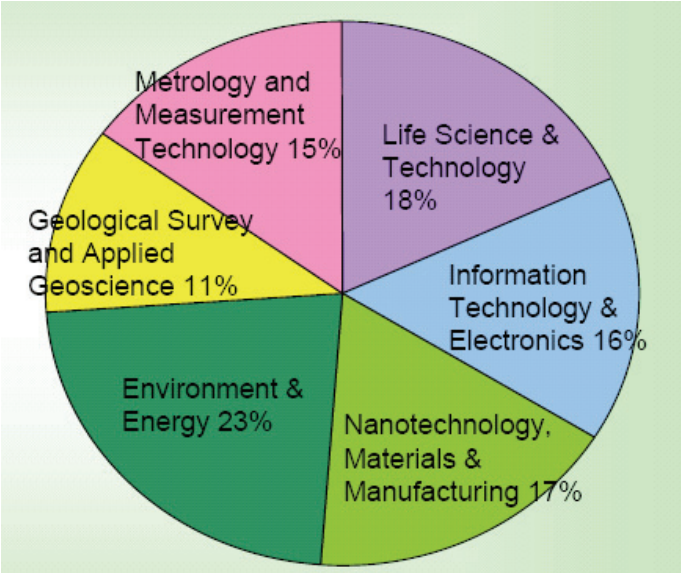

Figure C.2. Percentage of research staff in the 6 key areas of AIST (http://www.aist.go.jp/index_en.html, courtesy of AIST).

In the Environment & Energy theme at AIST, catalysis is important in 3 research centers (Biomass Technology, Hydrogen Industrial Use and Storage, and New Fuels and Vehicle Technology) and 2 research institutes (Innovation in Sustainable Chemistry, and Energy Technology). During the WTEC team's visit to AIST in Tsukuba, we met with researchers in Innovation in Sustainable Chemistry and New Fuels and Vehicle Technology.

AIST has a large number of visiting researchers and encourages international collaboration. The number of visiting researchers at AIST for FY2006 includes 600 postdoctoral researchers, 950 researchers from private companies, 2000 from universities, 900 from corporations, and 850 international researchers. AIST has a variety of support for foreign researchers working or staying at AIST, including offices, guesthouses, and introduction to Japanese language and culture. Several start-up companies have spun-off based on research in AIST. In FY2005 there were 20 venture companies that originated from AIST. So far there have been some 80 start-ups established since the start of the new AIST in April 2001.

The research bases for the Institute for Innovation in Sustainable Chemistry (ISC) are at Tsukuba and Kansai (Osaka). The total budget for FY2006 for ISC was $18.2 million. ISC consists of a staff of 191 that includes 86 scientists, 2 administrative staff, 35 postdoctoral researchers, 60 technicians, and 8 secretaries. The staff is primarily Japanese, except for 3 Chinese, 1 Korean, and 1 Indian.

The missions of ISC are to use technology based on chemistry and chemical engineering to:

1. Minimize toxic emissions and waste materials
2. Maximize energy efficiency
3. Maximize renewable resources

RESEARCH AND DEVELOPMENT ACTIVITIES

ISC contains many research activities. Some of the research activities that were discussed during the WTEC team's visit are noted below.

Selective Oxidation

ISC is studying methods for oxidative conversion of petroleum-based materials to chemicals. The goal of this technology is to reduce energy consumption and toxic reagents such as halogens and heavy metals. ISC is conducting research for selective oxidation with oxygen and H_2O_2. Its researchers have developed an Au-based catalyst that can produce propylene oxide (from propylene, O_2 and H_2) with a 90% selectivity (Figure C.3). The probable reaction route involves a mix of the Au and Ti-Si-oxide support. ISC has also developed a halide-free synthesis method to produce insulating resins. It is developing other methods for "clean oxidation" using H_2O_2 to produce intermediates for synthetic fibers and pharmaceuticals. ISC is now expanding to more difficult selective oxidations, such as the production of unsaturated aldehydes.

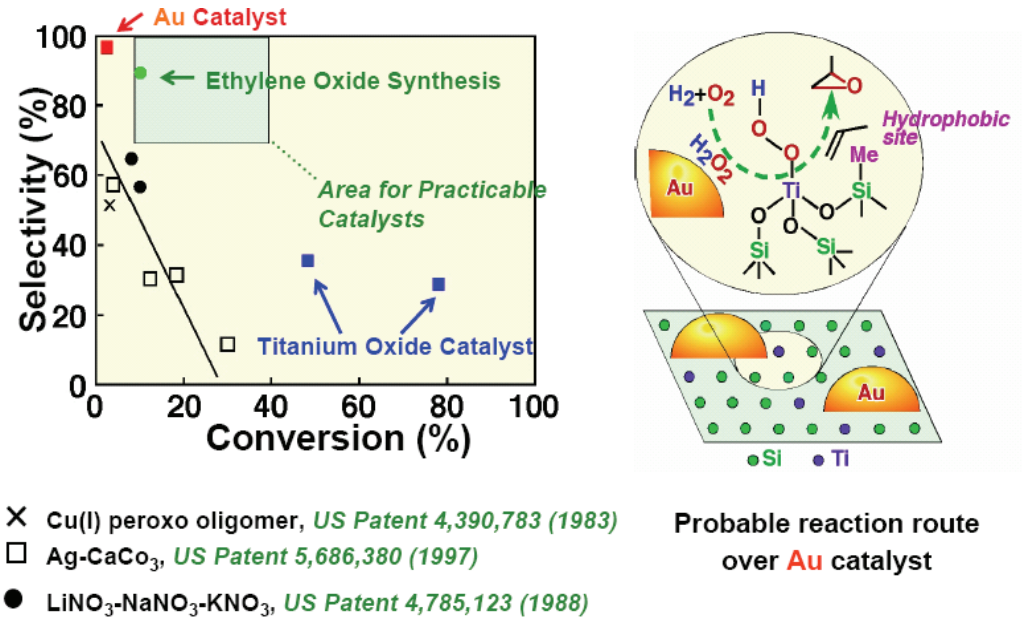

Figure C.3. Propylene oxide production on Au-based catalyst (Chowdhury et al. 2006).

New Synthesis Method of Organic Carbonates from CO_2

ISC is developing new synthesis methods of organic carbonates from CO_2. Carbonate production typically involves the use of highly toxic and corrosive phosgene, which requires chlorine (Cl_2). AIST is developing a process to produce carbonates from CO_2 and alcohols. They are focusing on the development of efficient catalysts for this process.

Automotive Exhaust Catalysts

Emission vehicle regulations are becoming increasingly strict in Japan, and there is a need to develop new technology to reduce NO_x and PM emissions. The research subjects in terms of automotive catalyst have to do with the following:

1. Selective reduction of NO with reducing agents (i.e., hydrocarbons, H_2, or CO)
2. Selective reduction of NO with ammonia

3. NO_x traps and direct NO decomposition
4. Development of three-way catalyst with low platinum group metal loading

A fundamental and applied research program is being undertaken on the catalytic removal of NO_x in exhaust emissions. ISC researchers have successfully developed alumina-based catalysts that can reduce NO_x using hydrocarbons as reductants. They have developed a practical catalytic system that can apply this to stationary diesel engines. They are now investigating NO_x reduction by H_2 or CO. Figure C.4 shows the regeneration model of active catalytic sites over Ir via SO_2 adsorption, dissociation, and desorption in the Ir-catalyzed NO_x reduction system by H_2 or CO. They are also studying the direct decomposition of NO_x without a reducing agent.

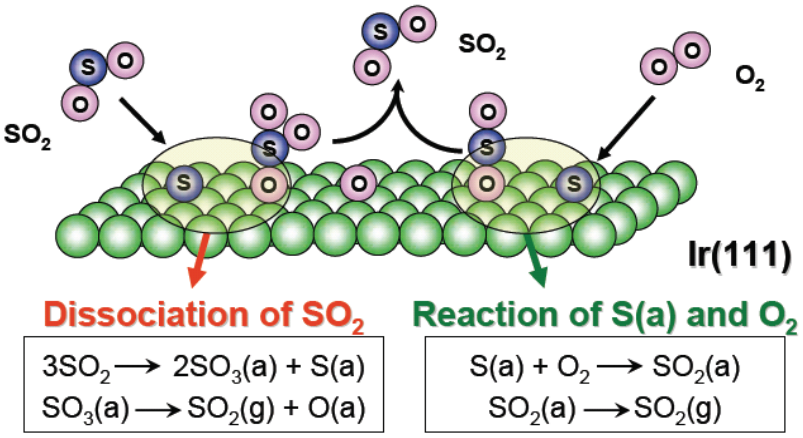

Figure C.4. Chemistry of SO_2 over Ir-based catalysts (Fujitani et al. 2007).

Theoretical Studies on the Absorption Spectra of Ruthenium Polypyridyl Dyes for Nanocrystalline TiO_2 Solar Cells (Kitao and Sugihara 2007)

AIST is studying dye-sensitized solar cells, which include oxide semiconductor photo-electrodes, sensitizing dyes, and redox electrolytic solutions. These dye-sensitized solar cells are cheaper than silicon solar cells and offer promise in terms of next-generation solar cells. Time-dependent density functional theory is being used to study the absorption of ruthenium polypyridyl dyes in water and ethanol. The shape of the calculated spectra is similar to the experimental spectra over the entire visible region (Figure C.5). This type of analysis can explain the details of the absorption spectrum. It is expected that this analysis will be useful for the synthesis of new sensitizers for high-performance dye-sensitizing solar cells.

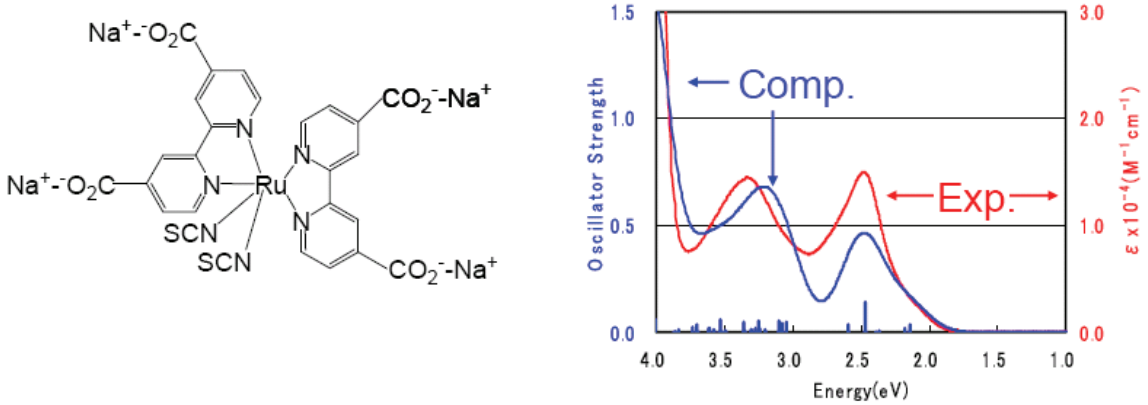

Figure C.5. Measured (red) and calculated (blue, TD-DFT-Gaussian) absorption spectra of dye N719 (structure of N719 is shown on the left) in 0.01 M aqueous NaOH.

Other catalysis-related research activities in AIST:

1. Hydrotreating catalysts
2. Reforming gas to liquids
3. Reforming biomass to liquids
4. Preferential CO oxidation with Au-based catalysts
5. Catalysis on fuel cells
6. Photocatalysts

SUMMARY AND CONCLUSIONS

Catalysis is currently a central theme in many of the projects within AIST. There are also many Japanese industries that benefit from the fundamental and applied catalysis research done at AIST. As AIST focuses more on a sustainable society, it is likely that catalysis will continue to be critically important to its mission.

According to our hosts at AIST, the future directions of catalysis include

1. Integration of catalytic technology with other technologies, e.g., microreactor, microwave, ionic liquids, and membranes.
2. Highly selective catalysts, e.g., oxidation, C-C coupling, chiral synthesis
3. Expansion of raw materials from petroleum and ethylene to natural gas and biomass
4. Substitution of noble metals with cheaper substitutes

AIST scientists also believe that heterogeneous catalysis will move towards the idea of molecular catalysis with single-site catalysts, as illustrated in Figure C.6. Their view is that these newer-generation catalysts will be higher in activity but harder to design.

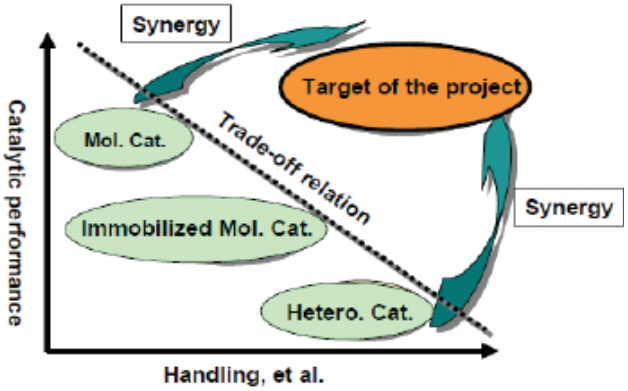

Figure C.6. Future direction of catalysis from heterogeneous catalysts to molecular catalysis.

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Fujitani, T., I. Nakamura, Y. Kobayashi, A. Takahashi, M. Haneda, and H. Hamada. 2007. Adsorption and reactivity of SO_2 on Ir(111) and Rh(111). *Surface Science* 601:1615-1622.

Kitao, O., and H. Sugihara. 2007. Theoretical studies on the absorption spectra of heteroleptic ruthenium polypyridyl dyes for nanocrystalline TiO_2 solar cells: Revisited with transition-component analysis. *Inorg. Chem. Acta* doi:10.1016/ j.ica.2007.05.051.

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Date Visited: June 7, 2007

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Prof. Longya Xu
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Prof. Zhijian Tian
Group leader Applied Catalysis

Dr. Yinxun Wei, Applied Catalysis

Many graduate students and post docs were also in attendance.

BACKGROUND

Dalian Institute of Chemical Physics (DICP) of the Chinese Academy of Sciences is a multidisciplinary institute devoted to both basic and applied research. DICP has the State Key Laboratory of Catalysis (SKLC) and State Key Laboratory of Molecular Reaction Dynamics (SKLMRD), and key national projects in Fuel Cells, Chemical Lasers, and Materials. Laboratories involved in applied research areas include analytical chemistry, fine chemicals, applied catalysis, and biotechnology. In addition, there are a number of spin-off companies for pesticide intermediates, membrane technology, chromatography, fuel cells, and catalysts. There are approximately 1500 staff (one-third in catalysis), 51 research groups, and nearly 800 graduate students.

Figure C.7. DICP campus in Dalian.

The SKLC has ten professors (one of whom is a member of the Chinese Academy of Sciences), about 40 graduate students, and 10 postdoctoral fellows. The emphasis is on fundamental research on the active phases of catalysts, active sites, and the mechanisms of catalytic reactions. Presently, the main areas in basic and applied research include the catalytic conversion of lower alkanes, environmental protection, and the catalytic synthesis of fine chemicals.

SKLC's primary areas of research are

- New catalytic reactions
- New catalytic materials
- New characterization techniques

The laboratory is equipped with up-to-date and advanced instruments, including high-resolution electron energy loss spectroscopy, X-ray photoelectron spectroscopy, Fourier transform Raman spectroscopy, ultraviolet resonance Raman spectroscopy, high-resolution magic-angle spinning NMR, photoelectron emission microscope, transmission electron microprobe, electron microscope, XRD, and automated chemisorption measurement. Special emphasis is placed on developing and employing *in situ* and transient techniques for catalyst characterizations.

RESEARCH AND DEVELOPMENT

DICP Energy-Related Projects

- Clean Coal Utilization
  - Air separation
  - Purification of syngas
  - Syngas synthesis, including FT
  - High-efficiency power from SOFC
- Liquid Fuel Substitution
  - GTL and MTG for gasoline
  - Ethanol from syngas
  - DME for diesel fuel
  - MTO for ethylene and propylene
- Alternative energy

- Fuel cells
- Biomass to liquid fuels and chemicals
- H_2 production by algae
- Solar energy for H_2 production

DICP Fundamental Research

- Selectivity control (chemo, shape, region, and enantiomeric)
- Model catalyst and reactions
- Photocatalysis
- Electrocatalysis
- Catalysis at the atomic, molecular, and nanometer scales
- Theoretical calculations

DICP Catalyst Preparation

- Nanoscale and highly dispersed catalysts
- Supported nanoparticles of noble metals
- Mixed oxide conducting membranes
- Zeolites and mesoporous molecular sieves
- Transition metal nitrides, carbides, and phosphides
- Chiral solid catalysts

DICP Catalytic Reactions

- Light paraffin upgrading
- Partial oxidation to syngas
- Direct conversion of CH_4 to aromatics
- Syngas to methanol and higher alcohols
- Methanol reforming to H_2
- Epoxidation of olefins (H_2O_2 and O_2)
- Asymmetric reactions on solids
- Environmental catalysts (NO_x, dioxin decomposition, CO oxidation, HDS)
- Photocatalysis (H_2O splitting to H_2 and O_2)
- Electrocatalysis (CO-tolerant catalyst for DMFC)

DICP Catalyst Characterizations

- *In situ* (FT-IR, NMR, UV Raman, Laser Raman, TPR, TGA-DTA)
- Dynamics and kinetics (PEEM, time-resolved spectroscopy, LISF, TPD-mass spec)
- Structure determination (XRD, SEM, TEM, EDX, BET)
- Atomic-, molecular- and nanometer-scale (HRTEM, XPS, AES, LEED)

SITE TOUR

- *Laboratory of Biotechnology*: It is engaged in conversion of cellulosic biomass to biodiesel fuel with oleaginous microorganisms..
- *SKLMRD*: It follows time-resolved methods of photocatalysis; its researchers have developed a method for surface detection; they are interested in splitting H_2O to H_2 and O_2.

- *Applied Catalysis*: One to two new processes are developed per year; examples include alkylation of benzene with FCC off-gas (to ethylbenzene) and MTO.
- *Advanced Chemical Engineering*: This is the catalyst development lab for the fuel cell group; it does reaction chemistry for SCR diesel, WGS, Prox, CO_2 capture; it is also actively developing fuel cell (alloy) catalysts tolerant for 20 ppm CO.
- *Fuel Cell*: This group is responsible for production of small to large (practical) fuel cells (PEM, SOFC, MeOH and EtOH, and micropower); the central problem is stability and durability
- *Fine Chemicals*: Reactions of interest include biomass to glycols, lubrication oils from olefins, and selective oxidation catalysts.
- *SKLC*: Reactions of interest include MeOH to acetic acid, enhanced active surface coating for TWC, PtFe bimetallic for CO oxidation; *in situ* characterizations include UV-Raman for zeolite synthesis, FT-IR, solid-state MAS (3 kHz) NMR (up to 250°C), Xe-excited laser for enhanced Raman sensitivity, and high-resolution (1 meV) EELS.

SUMMARY AND CONCLUSIONS

There is a large effort at DICP in new catalytic materials synthesis and applications. Much of the research is directed to development of new energy (MTG, FT, alcohols, fuel cells, etc.) for the growing national economy. DICP also conducts many projects sponsored by industry. There is a large research effort in nano-metal synthesis for fuel cells, and a significant effort in synthesis and applications of zeolites. The majority of research at DICP and SKLC is directed at applied projects, with 1–2 new commercial projects each year, including the formation of start-up companies that have spun off from previous research activities; nevertheless, there are many state-of-the art instruments for catalyst characterization. The laser lab is highly noteworthy, with *in situ* Raman studies and multiphoton fast acquisition methods on photocatalysts. Also, the *in situ* MAS NMR analysis is novel, with good potential for an important new characterization method in the coming years.

Site: **Dalian University of Technology (DUT)**
No. 158 Zhongshan Road
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http://www.dlut.edu.cn/dut-e/main.htm

Date Visited: June 7, 2007

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BACKGROUND

Dalian University of Technology (DUT), founded in 1949, is a relatively young university, but it has become one of the 26 key national universities in China. It encompasses a State Key Laboratory of Fine Chemical Engineering and the Key Laboratories of Petrochemical Technology and Equipment and of Biochemicals. School of Chemical Engineering has 67 professors, 90 associate professors, 342 PhDs, and 1200 MS-level students in 7 different departments. The catalysis effort is distributed among these departments. In addition, the Institute of Industrial Catalysis has 8 full and 3 associate professors, 2 lecturers, one senior engineer, 3 junior engineers, 30 PhDs, and 120 MS-level students. A major theme of catalysis research at DUT involves the synthesis of "green" fine chemicals.

RESEARCH AND DEVELOPMENT

The research at the institute has both applied and basic research components as explained below.

Synthesis of Molecular Sieves

A combination of impregnation, deposition, plasma technology, and nanocasting is used to create nanostructured catalyst materials (Figure C.8). Molecular sieves such as ZSM-5, nanocrystalline-ZSM-5, Beta, MCM-41, Ti-MCM-41, TS-1, and TS-2 are used both as catalysts and as catalyst supports for metal particles. Synthesis of carbon nanotubes is also being researched at DUT. The following reactions are examples of how the research on molecular sieve catalysts is being applied.

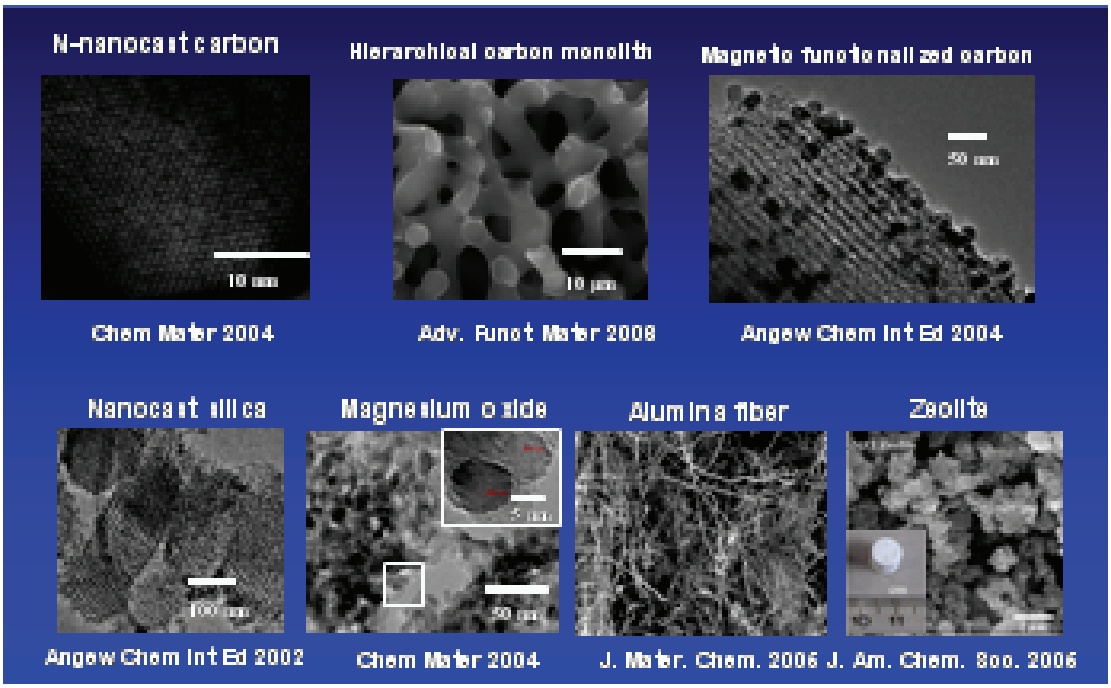

Figure C.8. Examples of new structures created at DUT by nanocasting (source: presentation by Prof. Wencui Li).

Alkylation

The alkylation of benzene and related aromatic compounds over modified ZSM-5 (comprehensive modification is achieved by mixing rare earth, P, Mg, and hydrothermal treatment) has been commercialized. The alkylation of benzene with propylene over modified Beta zeolite catalyst has also been tested for 7000 hours, and no appreciable decrease in activity has been observed. The conversion of ethylbenzene is about 15 wt% and the selectivity to para-diethylbenzene is above 98%. Another example includes the alkylation of toluene with methanol over modified ZSM-5 (28% conversion of toluene has been demonstrated) to selectively produce para-xylene (for run time of about 300 hours).

Oxidation

Epoxidation of propylene with H_2O_2 over TS-1 in a fixed-bed reactor results in conversion of 95% and about 95% selectivity to propylene oxide, while 98% PO selectivity is obtained by gas-phase epoxidation of propylene in the presence of H_2 and O_2 over Ag/TS-1, at 2.1% conversion.

Olefin Reduction in Gasoline

Most gasoline in China is obtained by the FCC process, and it contains about 40% olefins. Modified nanocrystalline-ZSM-5 catalysts are being tested for the reduction of olefins in gasoline.

Desulfurization

Micro-mesoporous TS-1 is used for desulfurization by oxidative removal of S from FCC and coal liquefaction products.

Research in Energy and the Environment

China has adopted the European standards for energy production and green house gas emissions. Research projects to meet these standards include production of ethanol from corn, use of oil shale to extract crude oil,

CO_2 utilization by synthesizing cyclocarbonate and polycarbonate compounds, artificial photosynthesis by biomimetic Fe complexes, thermal regulated hydrogenation, and molecular recognition and chemosensors.

A pretreatment transient reaction product analysis method is applied to understand the intermediate species on the surface during the selective catalytic reduction of NO_x with C_2H_4 over Co-ZSM-5 catalyst. The direct experimental evidence shows the existence of hydrogen on the surface intermediate species. The composition and concentration of surface intermediate species $NC_aO_bH_c$, formed by the pretreatment of Co-ZSM-5 in a $NO/C_2H_4/O_2$ gas mixture at 275°C, have been determined qualitatively and quantitatively. *In situ* DRIFT measurements reveal the coexistence of N-H, C=O, C-N and C-H species formed on the Co-ZSM-5 catalyst surface under the standard three component pretreatment (Figure C.9). DFT and Morse potential calculations are used to model the surface adsorption energies for $NC_aO_bH_c$ species.

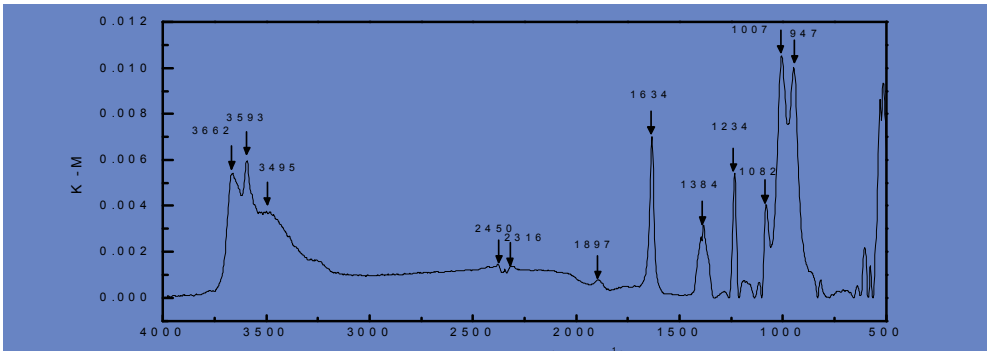

Figure C.9. *In situ* DRIFT study on the surface species formed under the standard three component pretreatment confirms the coexistence of N-H, C=O, C-N and C-H bonds on the Co-ZSM-5 catalyst (source: presentation by Prof. Chuan Shi).

SUMMARY AND CONCLUSIONS

The catalysis program at DUT aims at solving energy- and pollution-related issues. Efforts are directed towards a combination of basic and applied research. Novel nanostructures have been synthesized for polymerization, alkylation, oxidation, and CO_2 sequestration processes. The DUT research is supporting commercial plants for super-low-temperature (77 K) polymerization. Most of the funding comes from national sources such as Natural Science Foundation of China and industry.

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Zhao, J.Z., M.G. Davidson, M.F. Mahon, G. Kociok-Köhn, and A.D. James. 2004. An enantioselective fluorescent sensor for sugar acids. *J. Am. Chem. Soc.* 126:16179-16186.

Site: **Hitachi High-Technologies Corporation**
Naka Application Center
Advanced Microscope Systems
882, Ichige, Hitachinaka-shi
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Date Visited: June 7, 2007

WTEC Attendees: R. Lobo (report author), G.W. Huber, M. Neurock

Host: Dr. Takeo Kamino
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BACKGROUND

Hitachi High-Technologies is a subsidiary of Hitachi Corporation dedicated to the development and manufacture of scientific instruments for fundamental studies and for industrial applications. Hitachi High-Technology manufactures scanning electron microscopes (SEM), transmission electron microscopes (TEM), and scanning-transmission electron microscopes (STEM) that are among the best in the world. The company has recently decided to develop a suit of instruments especially designed for the needs of catalysis research.

The WTEC team first visited the manufacturing facilities, where we were received by technical and management staff of the company. After a brief introduction to the activities and markets of interest to the company, Dr. Kamino gave a talk about the research capabilities that Hitachi has developed in a new family of instruments, which could be of great help in research of heterogeneous catalysts. After his talk, the team toured the manufacturing facilities and then moved to the application center to observe the instruments obtaining images of model samples.

ELECTRON MICROSCOPES FOR CATALYSIS RESEARCH

Electron microscopy can accomplish the following functions in catalysis research:

- Structural analysis
- Chemical composition analysis
- 3D distribution of material in a sample
- Dynamic *in situ* observation at high temperature of the evolution of solid-state structures
- Synthesis of nanostructures and determination of their properties

From the WTEC team's perspective, what appears particularly promising is that a group of instruments, including sample holders and sample preparation units, has been developed as a system to address the items listed above. For instance, Hitachi High-Technologies has developed the first commercial dedicated STEM with a Cs-corrector (HD-2700 200 keV STEM). This instrument achieves a resolution of 0.14 nm and has a very high probe current that increases its sensitivity for chemical analysis. For instance, Figure C.10 shows a sample of PdTe on carbon in bright and dark field modes. This figure evidences the improved image quality and contrast achieved with this microscope.

Because of the high current of the electron probe, it is possible to obtain spatially resolved chemical composition information (using EDX) in a relatively short time (several minutes to obtain a complete image). Analysis of the spatially resolved composition information helps identify the uniformity — or lack thereof — of the sample.

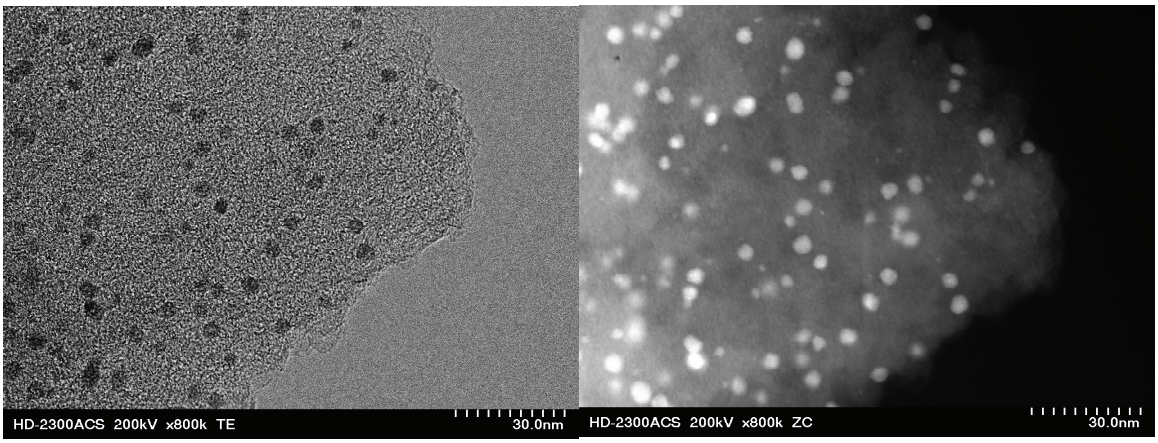

Figure C.10. Bright-field-STEM (left) and dark-field-STEM (right) images of PdTe nanoparticles on carbon.

Hitachi has also developed a suite of instruments specifically designed to obtain 3D images of chemically heterogeneous samples. These include a focused-ion-beam (FIB) milling system that automatically prepares samples in a geometry that can be analyzed using either a dedicated STEM or a TEM. It also includes a sample holder that is transferable between the FIB machine and either STEM or TEM instruments. This sample holder is designed to rotate the sample 360° in the specimen stage of the microscopes.

Hitachi has also developed a specimen-heating holder that uses a spirally wound tungsten filament that, because of its geometry, has very little drift as a function of temperature, keeping the sample in focus and allowing for high-resolution images at high temperature. By combining two of these filaments, it is possible to evaporate a metal (by evaporative heating) into a support, and in this form, to prepare model catalysts in the microscope. Figure C.11 shows a picture of one of these holders, and Figure C.12 shows two snapshots of the structure of gold nanoparticles deposited onto a model surface using this holder. Here one can see that while the gold is being deposited, atomic-resolution images can be obtained simultaneously.

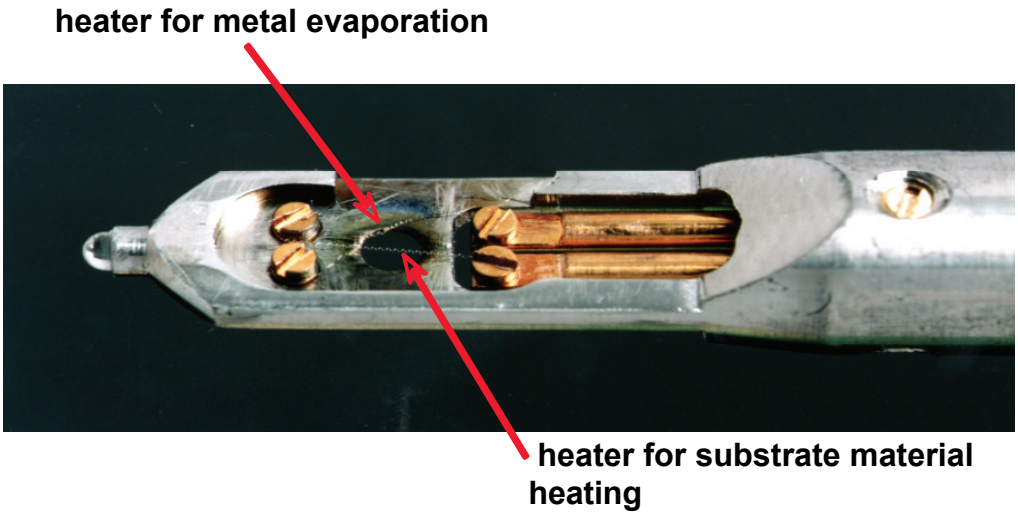

Figure C.11. Multifunctional heating holder equipped with two heating elements.

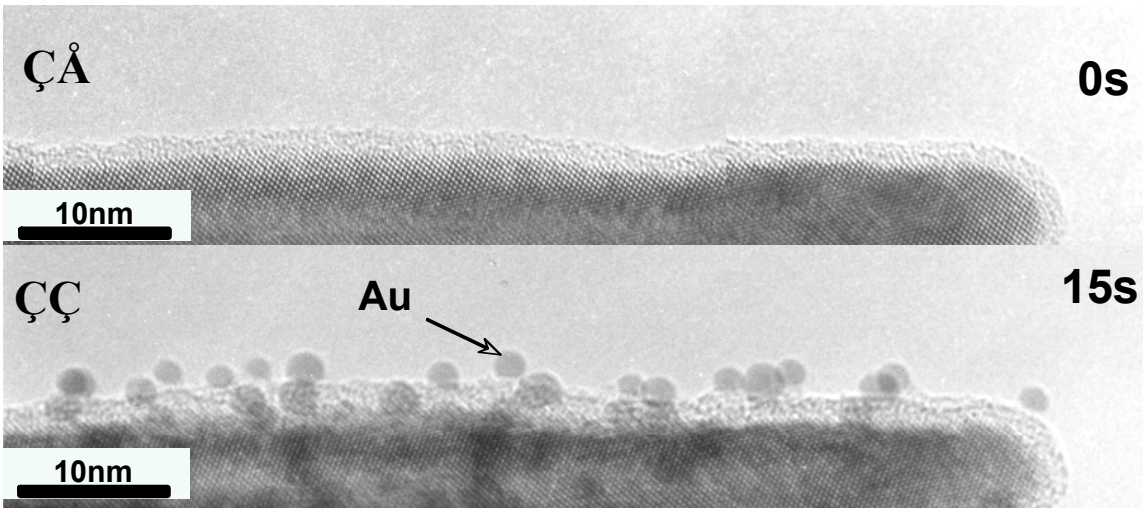

Figure C.12. *In situ* gold deposition onto the surface of a silicon particle.

Finally, Hitachi High-Technologies has developed a new 300 keV analytical microscope to carry out environmental TEM studies. This microscope has a specially designed column and evacuation system that allows for the feeding of gases onto the observed specimen while at the same time controlling the temperature. This can be done through the used of a differentially pumped-type environmental cell that allows for a pressure of up to ~ 0.1 Pa while maintaining atomic resolution.

Figure C.13 shows a sample holder that contains two heating elements and a gas injector that lets gases of a specified composition contact the solids deposited on the specimen heater. With this sample holder, for instance, one can deposit *in situ* a metal catalyst from the evaporator onto the surface of a catalyst support placed on the specimen heater. It is possible to control both the atmosphere and the temperature of this model material and investigate its structure while maintaining atomic resolution.

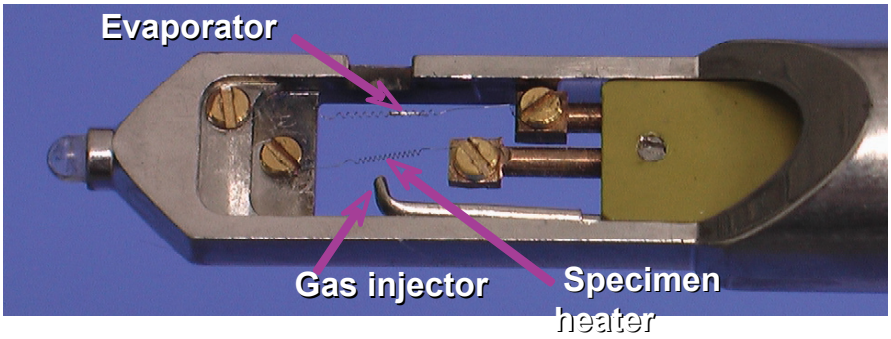

Figure C.13. Prototype of a gas-injection heating holder.

For instance, one can investigate a sample of PdAu nanoparticles supported on alumina as a function of temperature and gas composition. In Figure C.14, two nanoparticles of PdAu are observed at one million times magnification, in air (10^{-2} Pa), and at 420°C. It is possible to observe the dynamic behavior of such particles and determine if particle structure is stable under such conditions by observing coalescence of particles, segregation of particles into smaller units, or particle stability on a given support. All this can be done while controlling gas composition and pressure and the temperature of the sample. It is possible to foresee that a systematic use of these new technologies can be used to solve some of the long-standing questions in catalysis, such as mechanisms of catalyst deactivation or the nature of metal-support interactions under reaction conditions.

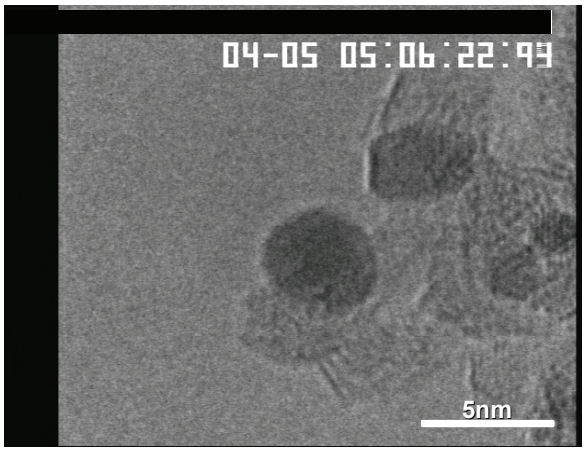

Figure C.14. Dynamic observation of PdAu particles on a alumina support investigated in an E-TEM in air at a total pressure of 10-2 Pa.

SUMMARY AND CONCLUSIONS

Environmental electron microscopy is bound to play an increasingly important role in elucidating the structure-property relationships of industrial heterogeneous catalysts. The routine use of these techniques in academic and industrial laboratories is not practiced because instruments capable of environmental conditions were simply not available from microscope manufacturers. Instruments such as the ones developed by Hitachi take us a long way towards making the daily use of environmental TEM a reality.

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Kamino, T., T. Yaguchi, T. Sato, and T. Hashimoto. 2005. Development of a technique for high-resolution electron microscopic observation of nanomaterials at elevated temperatures. *J. Elec. Microscop.* 54:205.

Site: **Hokkaido University Catalysis Research Center**
Kita 11, Nishi 10, Kita-ku
Sapporo 060-0811 Japan
http://www.cat.hokudai.ac.jp/index.eng.html

Date Visited: June 6, 2007

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BACKGROUND

Hokkaido University is one of the leading national universities of Japan. It was founded in 1876 as Sapporo Agricultural College by William S. Clark,[7] who was its first vice president. The college became Hokkaido Imperial University in 1918 as one of nine Imperial Universities. The School of Medicine was established in 1919, at which time the Agricultural College became the Faculty of Agriculture. This was followed by the Faculty of Engineering, the Faculty of Science, and finally in 1947, the Faculty of Law and Literature. The current name of Hokkaido University also came into use in 1947. In 1953, the Graduate School was established. Since 2004 the university has been incorporated as a National University Corporation under a new law that applies to all national universities. The University has 17 faculties in charge of undergraduate education and 17 corresponding graduate schools, with a total of ca. 6250 full-time faculty and staff members and 20,000 students at its downtown Sapporo campus.

Research in catalysis by nanostructured materials is conducted in the Catalysis Research Center (CRC), the only catalysis center in Japan. Fundamental research at CRC is sponsored by the Japanese government (e.g., JSPS, JST, etc.). CRC originated from the Institute of Catalysis founded in 1943 at Hokkaido University to conduct fundamental studies in catalysis. CRC started as a national collaborating institution in 1988, followed by its reorganization in 1998 to enable it to play a leading role in catalysis field and provide links for interdisciplinary research directions. CRC aims to construct a "total system" capable of analyzing reaction steps dynamically and creating catalysts and catalytic reactions via nano- and microscale assembly.

In 2007, CRC was internally reorganized into two areas: (1) the *Fundamental Research Division* consisting of six (soon to be seven) research sections where the efforts are devoted to constructing a new core of catalysis chemistry, and (2) the *Target Oriented Research Assembly* with several cluster-type organizations for promoting catalysis studies in collaboration with researchers in various fields of science and technology at other departments of Hokkaido University and at other national universities, research institutions, and industries. The CRC is home to 7 full, 7 associate, and 6 assistant professors, 40 postdoctoral researchers, 4 visiting professors, 19 collaborative researchers, 23 MS students, 22 PhD students, 13 temporary staff, and 8 permanent technical staff. CRC is actively engaged in international as well as national collaborations,

[7] Prior to founding Sapporo Agricultural College, Dr. Clark was a chemistry professor at Amherst College, a Massachusetts state senator, and 3rd president of the Massachusetts Agricultural College (now the University of Massachusetts Amherst).

maintains an office at Beijing University, and has set up joint laboratories in China at Peking University, Tsinghua University, China University of Petroleum, and East China Normal University.

RESEARCH AND DEVELOPMENT

Although there appears to be interesting research in the collaborative programs of the Target Oriented Research group, the WTEC panel's visit was focused on the activities of the CRC's Fundamental Research Division. Professor Ueda, the Director of the Catalysis Research Center, put together a well-organized and structured visit program consisting of introductions, brief tours of 4 laboratory facilities, short research presentations by six of the CRC laboratory directors, and 2 presentations by the WTEC panel members.

Section of Catalytic Materials Chemistry headed by Professor Ueda, is focused on catalytic oxidation over metal oxides represented by (1) selective alkane oxidation catalysis over multicomponent Mo-V oxides; (2) environmental catalysis for the decomposition of NO_x, particulate emissions and organic wastes employing catalytic SiC fibers supporting undoped and doped ZrO_2, YSZ, and some perovskite structures; and (3) fuel cells and oxidative energy conversion devices. This laboratory pioneered novel creative synthesis approaches employing molecular precursors to uniquely active and selective alkane oxidation catalysts based on Mo-V oxides. It also performed key studies aimed at unraveling the structural origins of their catalytic behavior.

Section of Catalytic Transformation, headed by Professor Fukuoka, is developing biorefinery concepts by heterogeneous catalysts. The research team recently discovered that Pt or Ru catalysts supported on inorganic oxides showed high activity for the highly desirable conversion of cellulose into sugar alcohols, mainly sorbitol and mannitol, in water under hydrogen pressure; furthermore, they discovered that the catalysts can be recycled over repeated runs. Glucose was produced in low yields, thus suggesting that the Pt (or Ru)/oxide works as a bifunctional catalyst for the hydrolysis of cellulose and subsequent reduction to sorbitol.

Section of Surface Structure Chemistry, headed by Professor Asakura, is interested in elucidating the structure and catalytic properties of oxide surfaces and to design well-defined oxide surfaces for new classes of catalysts. This laboratory has pioneered several new surface analytical techniques for real-time nanoscale surface images, including energy-filtered X-ray photoemission electron microscopy (EXPEEM), X-ray aided non-contact atomic force microscopy (XANAM), and polarization-dependent total-reflection fluorescence (PTRF) XAFS. Recent systems investigated by these novel techniques include Ni nanoparticles supported on TiO_2(110) and N_2O adsorption and decomposition over Pd(110).

Section of Molecular Catalysis Chemistry, headed by Professor Takahashi, is developing novel transition metal containing catalysts and processes for selective C-C bond cleavage/formation or interesting stereoselectivity. Recent examples include a novel reaction of forming indene derivatives from a titanocene species, and an asymmetric kinetic resolution of a planar chiral ferrocene by Mo-catalyzed metathesis, which is a rare example of catalytic asymmetric induction of planar chirality in metallocenes.

Section of Interfacial Spectrochemistry, headed by Professor Osawa, is focused on studies of reactions at interfaces at molecular scale employing IR, surface-enhanced IR (developed in this laboratory), Raman, IR-Vis, sum frequency generation (SFG), STM, AFM and electrochemical techniques for μsec time-resolved characterization of electrocatalytic phenomena for fuel cell applications.

Section of Catalytic Reaction Chemistry, headed by Professor Ohtani, aims at developing more energy- and resource-efficient catalytic processes, focusing on the fundamentals of photocatalysis, as well as the synthesis and characterization of novel core-shell photocatalysts based on silica-coated CdS and CdSe nanoparticles.

SUMMARY AND CONCLUSIONS

The Catalysis Research Center at Hokkaido University is a world-class catalysis research institution university with significant activities in both fundamental and applied catalysis research. The CRC research laboratories pursue a number of highly innovative research directions aimed at understanding the fundamental steps underlying the catalytic phenomena and translating this knowledge to synthesis of novel

nanostructured catalytic materials. The Laboratory of Catalytic Reaction Chemistry successfully blends experimental research with quantum chemical theory of catalysis. The physical infrastructure and characterization facilities are outstanding, and the financial support for catalysis research is impressive.

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Hokkaido University homepage (English). n.d. http://www.hokudai.ac.jp/en/index.html.

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Date Visited: June 6, 2007

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BACKGROUND

The Institute of Coal Chemistry (ICC) is one of the research and development institutions affiliated with the Chinese Academy of Sciences (CAS), an organization dedicated since its founding in 1949 to sustaining and advancing China's science and technology infrastructure to world-class standards in support of the nation's social and economic development. The Institute of Coal Chemistry conducts basic and applied research in utilization of clean coal to meet China's needs for sustainable energy. The ICC has 270 research staff, 260 assistants, and 320 graduate students. The institute is authorized to grant advanced degrees. First-year graduate students attend classes at a remote university and return to ICC to complete their advanced degrees.

Figure C.15. The main ICC building.

ICC has 3 laboratories (Clean Coal Technology and Synfuels, Advanced Materials, Catalysis and Green Chemical Processes) and 4 engineering centers (Coal Gasification, Synfuels via FT, Carbon Fibers, Engineering and Chemical Processes). Its primary research areas are

- Gasification and C1 synthesis
- Pyrolysis and clean combustion
- Hydrogen and carbon dioxide

RESEARCH AND DEVELOPMENT

ICC has several large pilot/demonstration units in operation. There is a 100 tons/day low rank coal, fluidized bed gasification plant for production of syngas. A higher-pressure process is under development for higher capacity. The syngas produced from coal will be converted to Fischer-Tropsch (FT) liquids. ICC has a large Fe FT slurry demonstration unit (with the syngas produced from decomposition of methanol) (see right side, Figure 6.10).

ICC researchers have developed new, highly active Fe catalysts by DFT modeling of the active iron-carbide phases. Once the most active phase was identified, synthesis methods were developed to maximize this structure. The resulting new catalyst is two to three times more productive than previous catalysts. The active phase of Co FT catalysts has been located within the pores of the mesoporous support. The restricted pores size limits chain growth to the dimensions of the pores, leading to higher yields of liquid products. Additionally, higher alcohol catalysts composed of MoS_2 are under development since coal syngas may contain low levels of sulfur. Synthesis of methanol from CO_2-rich syngas is under investigation. Potential uses of methanol are production of olefins, aromatics, and gasoline.

ICC has a large program in nanosized environmental catalysts, e.g., selective reduction catalysts (SCR), which operate at high (metal/alumina) and at low temperatures (metal/carbon). ICC is looking at the feasibility of CO_2 sequestration by studying the swelling of coal, gas permeability, and extraction by supercritical CO_2. In addition, nanosized Ni-CaO-ZrO_2 (mesoporous support), which minimized carbon deposition during CO_2 reforming, is being investigated.

Prof. Wang leads the modeling group with modeling capabilities for Monte Carlo, molecular dynamics, *ab initio*, density functional, and quantum mechanics simulations. The topics of study include adsorption, diffusion and reaction in zeolites, catalyst design for higher alcohol synthesis ($NiMoS_2$), and active site and reaction mechanism of Fe FT catalysts.

SUMMARY AND CONCLUSIONS

ICC is investigating several potential routes for production of syngas to clean fuels and chemicals from coal. ICC has little work devoted to direct liquefaction of coal. Along with coal conversion technologies, ICC is developing technologies for the protection of the environment from SO_x, NO_x, and CO_2 emissions. Key to all these processes are new catalytic materials; one strategy for new catalyst synthesis is to model the optimum active site and subsequently develop methods for preparation of that structure. While focused on coal conversion processes and materials, there is some work on understanding the fundamentals of catalysis, especially in zeolites and mesoporous supports. Modeling along kinetic studies of model compounds gives insight into catalyst behavior.

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Date Visited: The WTEC team did not visit Jilin University in person but rather met with Professor Xiao at the Jade Palace Hotel, Beijing, on June 4, 2007.

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BACKGROUND

Jilin University is China's largest university, with approximately 70,000 students, 8 campuses, 39 colleges, 16 academic disciplines, 5 national key laboratories, 8 national bases for the development of basic science, and 18 other important scientific laboratories. The State Key Laboratory for Inorganic and Preparative Chemistry was opened at the Jilin University campus in 2001.

State Key Laboratory for Inorganic Synthesis and Preparative Chemistry

The Inorganic Synthesis and Preparative Chemistry lab at Jilin University was established in 1993 and opened officially with the current name in 2001. The 27 scientific staff members include 14 professors, 4 associate professors, 2 lecturers, and 7 engineers or technicians; the scientists are all renowned in China, and thirteen are members of the Chinese Academy of Sciences. The lab has 250 undergraduate students, 200 graduate students, 4 research groups, and 1 group of 35 in catalysis research. This laboratory is active both nationally and internationally. It organized the International Symposium on Solid State Chemistry in China in 2002 (ISSSCC-2002); the seventh International Hydrothermal Reaction Symposium (ISHR-7) in 2003; and it will preside over the 15th International Zeolite Conference in August 2007.

The lab is instrumented with new electron microscopes (HRTEM and SEM), single crystal X-ray diffractometers and high-throughput XRD, BET, IR, UV-Vis, Raman, NMR, and ESR spectrometers for catalyst characterization. In addition, the lab has over 1200 autoclaves for catalyst synthesis, high-pressure catalytic reactors, and 20 catalyst testing units with on-line gas chromatographs.

Research Areas

- Basic research of inorganic synthesis chemistry
- Synthesis of zeolites and mesoporous materials and their catalytic properties
- Development of new synthetic routes
- Computational synthesis and molecular engineering
- Green synthesis chemistry
- Biotic synthesis chemistry

Recently, research emphasis has been placed upon inorganic combinatorial chemistry, computation-assisted inorganic synthesis, hydrothermal and solvo-thermal synthesis chemistry, new microporous and mesoporous compounds and related single crystals, low-dimensional phosphates, solid ionic conductors,

photoluminescent and electroluminescent materials, magnetic compounds and semiconductors, host-guest chemistry, and new catalysts.

RESEARCH AND DEVELOPMENT

The primary research interests of the Laboratory for Inorganic and Preparative Chemistry are synthesis of mesoporous and microporous, i.e., zeolites, solids. Microporous zeolites are crystalline, have strong acidity and high hydrothermal stability; thus they have been widely used in commercial applications. Mesoporous materials are amorphous and have poor hydrothermal stability; thus they have limited commercial applicability.

Professor Xiao's group at Jilin University has explored several routes to stabilization of mesoporous materials. One approach is to first synthesize nano-alumino-silicate zeolite crystals, which subsequently are assembled into mesoporous arrays (Figure C.16). These mesoporous zeolites display higher activity and stability compared to the traditional zeolite or mesoporous catalysts, for example, alkylation of butene with isobutane with mesoporous-beta zeolite catalysts. Mesoporous titanosilicate catalysts also have been synthesized from nanoscale TS-1. For hydroxylation of phenol with hydrogen peroxide, the activity and selectivity are similar to TS-1. However, for hydroxylation of bulky molecules like trimethylphenol, TS-1 is inactive, while mesoporous TS-1 has high activity even compared to (nonzeolite) Ti-mesoporous catalysts. The increased activities, especially for bulky reactants, and higher stability are novel catalytic properties that may lead to new applications.

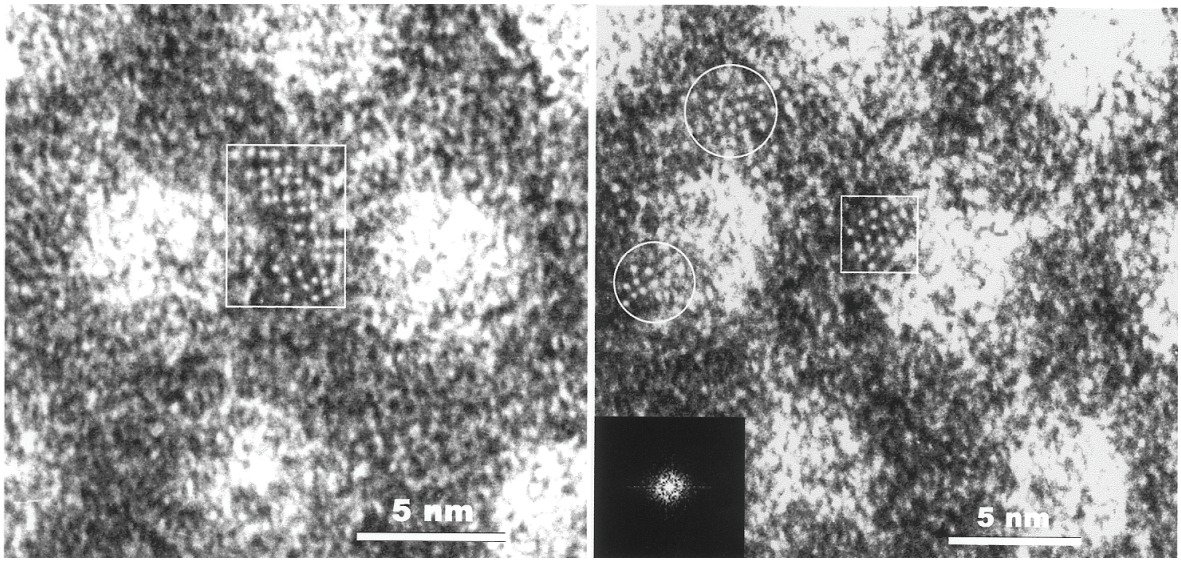

Figure C.16. Electron micrograph showing the mesoporous structure of about 5 nm diameter and smaller domains of aluminosilicate, nanoscale zeolite nanoclusters (highlighted by square and circles) (courtesy of Jilin University, Dr. Feng-Shou Xiao).

Another research area at Jilin is devoted to development of hydrothermally stable mesoporous solids. It is thought that instability results from the defect silanol sites, as evidenced by ^{29}Si MAS NMR, formed during the low temperature synthesis. At high temperature, however, the template micelle formation is unstable, leading to amorphous products. This lab has developed a family of high-temperature stable micelles, leading to hydrothermally stable mesoporous catalysts. Additionally, stable mesoporous materials have been synthesized with mixed templates like P123 and tetrapropylammonium ion. Although these mesoporous catalysts have much improved stability, they are less hydrothermally stable than zeolites. This group at the key lab has investigated methods to synthesize zeolite crystals, which additionally contain mesopores in the crystals. The approach is to add a cationic polymer during crystallization. Zeolites BEA and MFI have been successfully prepared. In the alkylation of benzene with isopropanol, the mesoporous BEA displayed higher

initial activity and better stability. Mesoporous zeolites also displayed high activity for bulky reactants. While there is little activity for cracking of triisopropylbenzene in MFI, high conversions were obtained with mesoporous MFI.

Finally, the Jilin group is exploring the incorporation of enzymes into mesoporous catalysts for both chemical and bio-chemical synthesis. During the synthesis, the enzyme is used to template macropores in silica. In addition, the silica prevents aggregation of the enzyme and allow for easy recovery from the products. Stable activity of trypsin for approximately 30 catalytic cycles was demonstrated.

SUMMARY AND CONCLUSIONS

A number of important industrial reactions utilize zeolite catalysts. Incorporation of mesopores into the zeolite catalysts lead to a number of important improvements, i.e., higher activity and stability. In addition, bulky reactants that typically do not react over zeolites may show high activity when the mesopores are combined with the zeolite. Two synthetic routes have been developed: synthesis of nanozeolites with subsequent synthesis of the mesoporous structure, and direct incorporation of mesopores into the zeolite crystal by utilization of cationic polymers. In order to better utilize mesoporous materials, higher hydrothermal stability is required. Significant progress has been made in this area by developing micelle templates that allow for higher synthesis conditions. These may be used as catalysts directly or be useful as supports for metal catalysts, for example. Finally, synthetic methods are being developed to support enzymes in mesoporous silicas. These will allow for better dispersion, easier recovery, and better diffusion of reactants and products. The WTEC team saw these concepts and materials being incorporated into applications throughout China.

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BACKGROUND

The Korea Advanced Institute of Science and Technology (KAIST) was established on December 31, 1980, through a merger of the Korea Advanced Institute of Science (KAIS, established in 1971 in Seoul) and the Korea Institute of Science and Technology (KIST). KAIST was transferred in 1989 to the Daedeok campus in Daejon, which is about 150 km south of Seoul. The Daedeok Science Town in which KAIST resides is also home to more than 60 research institutes, 4 universities, and numerous venture businesses. KAIST employs 296 professors, 72 associate professors, 52 assistant professors, and 34 research professors. The student enrollment in BS, MS, and PhD programs is 3021, 2042, and 2273, respectively, in the 4 colleges, 7 schools, 14 departments, and 6 divisions that comprise KAIST. The long-term vision of KAIST is to "become one of the best scientific and technological universities in the world, and as such, the region around KAIST will become a major hub for high-technology industries in Korea and the world." (KAIST brochure n.d.) The total effort in catalysis is the work of 3 professors in chemical engineering and 2 in chemistry, and their students. In the chemical engineering department, there are about 30 graduate students (10 MS and 20 PhD) involved in catalysis research.

RESEARCH AND DEVELOPMENT

The major research efforts in catalysis by nanostructured materials are centered in two labs at KAIST: the Center for Functional Nanomaterials directed by Professor Ryong Ryoo, and the Center for Ultra-microchemical Process Systems directed by Professor Seong Ihl Woo.

The Center for Functional Nanomaterials

KAIST's Center for Functional Nanomaterials was established 6 years ago as part of the National Creative Research Initiative in Korea. This particular center is funded at a level of $700,000/year through 2010. Every year, five new research centers are established after a country-wide competition in all fields of science. Although the funding for these centers is very flexible and lasts up to nine years, each center is evaluated on a 3-year cycle. Professor Ryoo currently works with 4 postdoctoral researchers, 7 graduate students, 4 undergraduate students, and 1 administrative assistant. Laboratory space is divided fairly evenly among all of the faculty members, but Professor Ryoo utilizes about 50% additional space because of the center activities.

The three main topics in the Ryoo laboratory involve (1) synthesis of mesoporous silica via supramolecular templating methods; (2) synthesis of nanostructured materials via "hard" templating methods, i.e. depositing carbon precursors into mesoporous silica and removing the silica phase (see Figure C.17); and (3) synthesis of zeolites with mesopores by designing new surfactant-based zeolite templates. The hard templating method has been used by the Ryoo lab to prepare well-structured mesoporous carbon material CMK-1, as illustrated in Figure C.18.

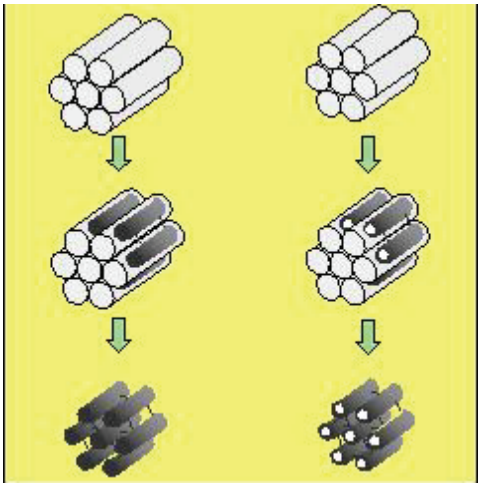

Figure C.17. Synthesis of nanostructured materials via the hard templating route. In this case, carbon precursors are deposited into the pores of mesoporous silica as rods or tubes. The silica "template" is removed to reveal a structured carbon material (courtesy of R. Ryoo).

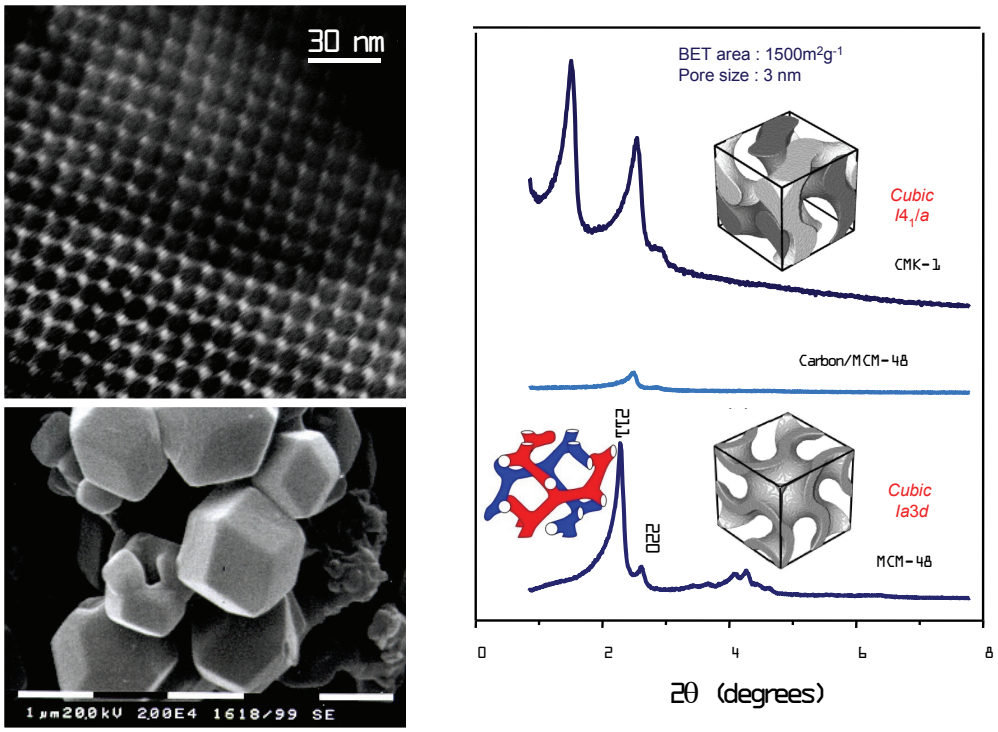

Figure C.18. Electron micrographs and X-ray diffraction patterns of mesoporous carbon CMK-1 (Ryoo et al. 1999).

In order to improve the transport and lifetime issues associated with zeolite catalysts, researchers around the world have attempted to introduce mesoporosity into the zeolite crystallites. Prof. Ryoo has synthesized mesopores directly into zeolites NaA and MFI by preparing a composite template with a silicon end group, a typical amine group used in zeolite synthesis, and a hydrocarbon tail that will form a micelle in the synthesis medium and therefore create mesopores in the sample. Figure C.19 illustrates the concept of the designed surfactant and a micrograph of mesoporous NaA zeolite. Catalytic reactions over mesoporous MFI compared to a traditional ZSM-5 catalyst revealed superior activity and stability of the new mesoporous system. This is an excellent example of how modifying the nanostructure of a catalyst by design can significantly improve activity and stability.

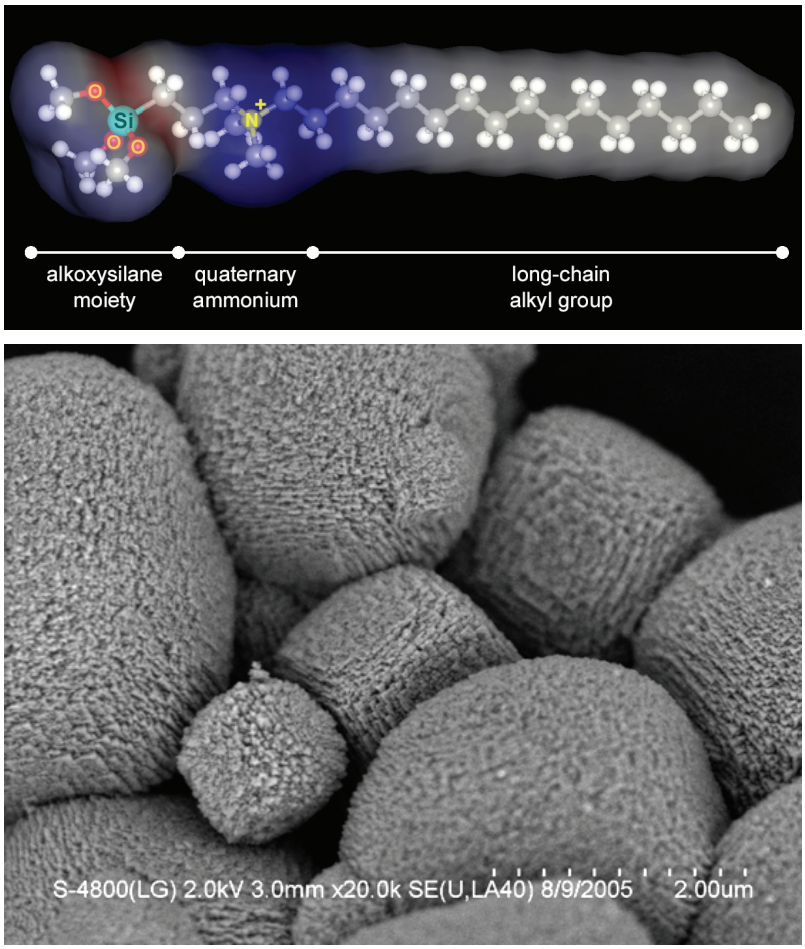

Figure C.19. New surfactant template (top) used to prepare NaA zeolite (bottom) with micro and mesopores (Choi et al. 2006).

Center for Ultra-Microchemical Process Systems

KAIST's Center for Ultra-microchemical Process Systems (CUPS) was established in 2001 and is directed by Professor Seong Ihl Woo. The main goal of the center is to design and manufacture chemical and biological process systems with nanometer to millimeter scales. The lab makes use of high-throughput screening methods to reduce the time to discovery of new materials. The tools used in the center include (1) a CombiAccelerator-I, a multitarget sputtering system that can make a thin film library of more than 5000 compositions on one substrate, (2) a CombiAccelerator-II, a multitarget co-sputtering system for making a continuous composition spread on a substrate, (3) a liquid source misted chemical deposition system, (4) A parallel polymerization reactor system consisting of 8 reactors, (5) a micro-Raman/UV-Vis fluorescence spectrometer, (6) a Bruker D8 Discover high-throughput X-ray diffractometer, (7) a parallel

stainless steel tubular reactor system consisting of 64 units with GC or MS detection of products, (8) a parallel quartz tubular reactor system consisting of 32 units capable of operating at temperatures exceeding 500°C. The vast array of high-throughput technology is used to develop new catalysts for olefin polymerization, deNO_x, oxidative dehydrogenation of light alkanes, oxygenation of hydrocarbons, photocatalysis, fuel cell electrodes, steam reforming, and CO_2 reforming.

SUMMARY AND CONCLUSIONS

The catalysis efforts at KAIST are focused in materials synthesis via templating (Center for Functional Nanomaterials) or via combinatorial deposition onto substrates (CUPS). The tools for characterization such as electron microscopy, diffraction, and adsorption are adequate for the world-class research performed in these centers. The experimental synthetic efforts are quite impressive. At the time of the WTEC panel's visit, there was very little theory and modeling work in catalysis at KAIST. Professor Woo indicated a desire to complement his efforts on high-throughput materials discovery with theory so that virtual composition libraries can be designed.

The graduate students are funded mainly by KAIST; additional external grant money for research has a very high value. Typical funding sources are the Korean Science and Engineering Foundation (KOSEF), the Ministry of Education, the Ministry of Science and Technology, and the Ministry of Economy and Industry. Although there is some support from industry (for example, Prof. Ryoo has a grant from General Motors in the area of emission control), the government is the main source of research support. The success rate of proposals at top institutions like KAIST is about one in three. In general, Korean graduate student quality is very high, but strong competition with the United States, Germany, Great Britain, and Japan for Korean postdoctoral researchers affects recruiting in Korea.

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BACKGROUND

The former Jing Shi Da Xue Tang (the Metropolitan University) of the Qing Dynasty was founded in December 1898; in May 1912 it was renamed Guo Yin Beijing Da Xue (National Beijing University), and today it is known simply as Beijing Da Xue, or "Peking University."[8] The University has 30 colleges and 12 departments, with 93 specialties for undergraduates, 2 specialties for the second Bachelor's degree, 199 specialties for Master's degree candidates, and 173 specialties for doctoral degree candidates. Currently Peking University has 216 research institutes and research centers, and there are 2 national engineering research centers, 81 key national disciplines, and 12 National Key Laboratories.

There are 60 groups and 400 graduate students in College of Chemistry. Most of the catalysis research is performed in this college and is directed towards nanomaterials synthesis and energy applications. The number of students admitted to the school is limited to maintain high education standards and each professor can accept only two new graduate students (one PhD and one Master's) every year.

[8] Peking University remains the institution's preferred English name, even though "Peking" is no longer used as the English name for the capital city of the People's Republic of China.

RESEARCH AND DEVELOPMENT

Nanocatalysis (Prof. Haichao Liu, College of Chemistry)

Prof. Liu's group is involved in evaluating the process of obtaining fuel and chemicals from biomass, CO_2, oil, coal, and methane via molecular catalysis (selective oxidation and hydrogenation). They are using nanosized particles of Cu/ZnO, Au, RuOx, and Ru/ZrO_2 for selective oxidation and hydrogenation (Figure C.20). Polyols (e.g., sorbitol, glycerol) obtained from biomass (e.g., cellulose) are being explored as feedstocks for hydrogen and hydrocarbon production via aqueous phase reforming. Moreover, polyol conversion to chemicals via hydrogenation and hydrogenolysis is also being explored. Prof Liu's lab has a high-pressure and multifunction reactor. He is using hydrogen TPR, *in situ* FTIR, GC, mass spectroscopy, Raman, XRD, and TEM for characterization of catalyst structure and properties (activity and selectivity). Prof. Liu is also involved in modeling structure and chemical interactions of catalyst particles in solution.

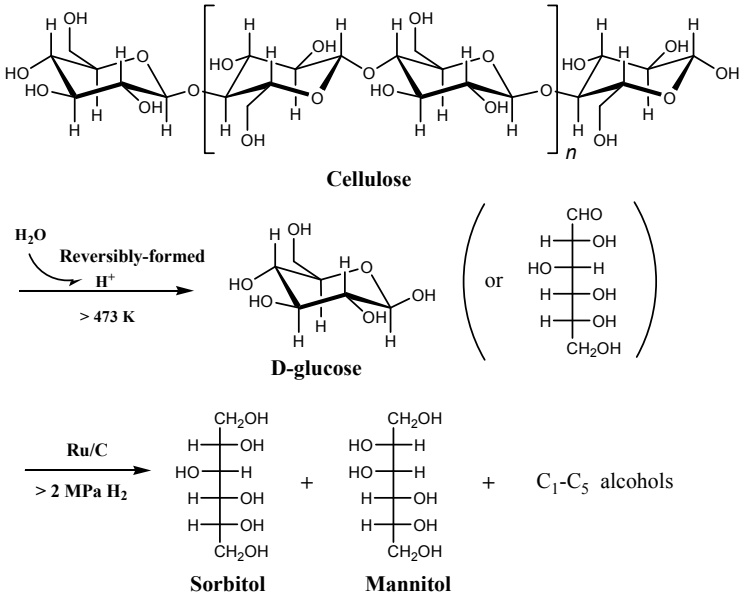

Figure C.20. Catalytic cellulose conversion to polyols.

Green Catalysis in Ionic Liquid and Water Phase (Prof. Yuan Kou, College of Chemistry & Molecular Engineering)

Prof. Kou is investigating the performance of soluble nanoparticles for catalytic generation of energy using alcohol as a fuel (green catalysis). He is using ionic liquids (IL) for selective dissociation of biomass products (cellulose and lignin) into fuels and chemicals (Figure C.21). Ruthenium catalyst particles in ionic liquids have been successfully used for selective cleavage of C-O bonds in cellulose to produce C6-carbohydrates. The process relies on nanocluster catalyst particles dissolved in functionalized ionic liquids to lower the reaction temperature. His group has invented a new soluble nanocluster catalyst (Pt NCs), that is highly stable and can catalyze the aqueous-phase aerobic oxidation of a wide range of activated and nonactivated alcohols, including aromatic, allylic, (primary and secondary) aliphatic alcohols, and alicyclic alcohols, with high efficiency and without being deactivated after long-term use. IL-based catalysis can also be used for oxidation of CNB, alcohols, and Fischer-Tropsch synthesis (FTS). Prof. Kou is also evaluating the effect of adding a small amount of water (1%) to the carbon precursors on the selective synthesis of SWCNTs using an Fe catalyst.

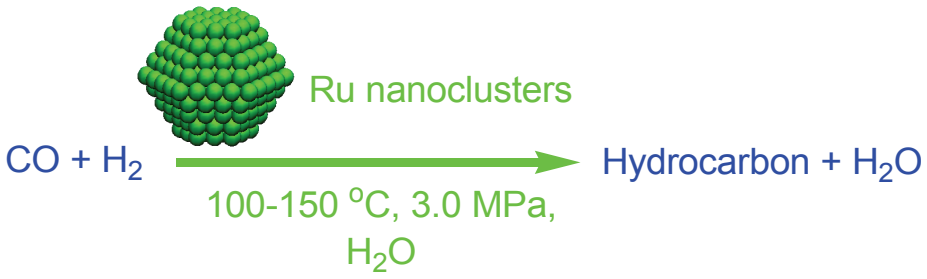

Figure C.21. Aqueous-phase F-T synthesis on soluble Ru nanocluster catalyst.

Synthesis of Metal Nanoclusters (Prof. Yuan Wang, College of Chemistry & Molecular Engineering)

Prof. Wang's group is involved in synthesis and characterization of "unprotected" nanosized (0.7–2 nm) metal clusters with 13 to 147 atoms. The synthesis scheme and resulting particle size distribution is shown in Figure C.22. Bimetallic catalysts can also be synthesized using this scheme. These particles, stabilized with ethylene glycol and simple ions, have high preparation efficiency, small particle size, narrow size distribution, and high stability. They can be separated and modified easily and can be used as building blocks for the fabrication of functional systems. Their applications range from catalytic synthesis of various chemicals, anode material for SOFC, generation of rocket fuel, and sensors, to synthesis of magnetic and antistatic materials. Platinum nanoparticles show better performance than commercial catalysts in the selective hydrogenation of chloro-nitro benzene.

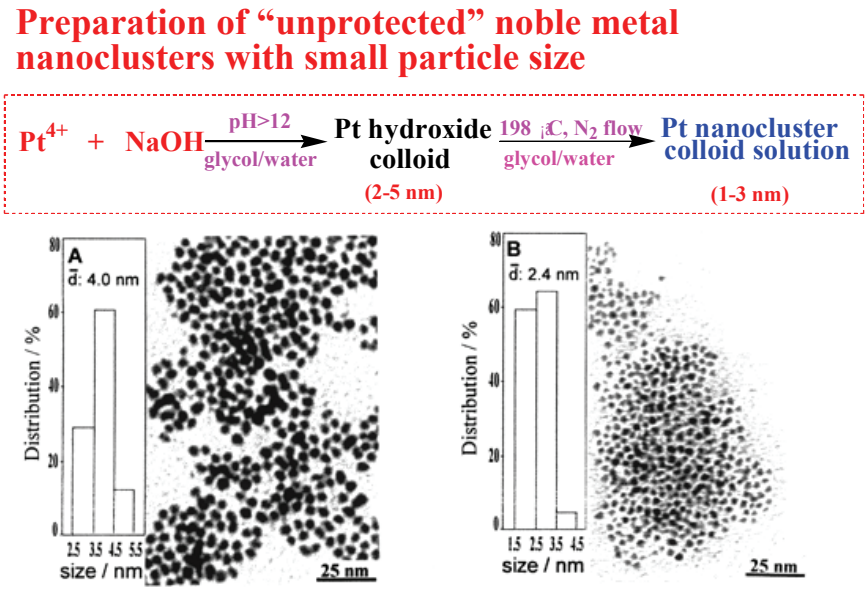

Figure 3. TEM photographs of the platinum hydroxide colloidal particles (A) in glycol/water (10/1) and the Pt cluster (B) derived from reduction of the Pt hydroxide colloid.

Y. Wang, et al, Chem. Mater. *12*, 1622, 2000

Figure C.22. Preparation of "unprotected" noble metal nanoclusters with small particle size.

Spontaneous Monolayer Dispersion and Its Applications (Prof. Xie Youchang, Professor of Physical Chemistry)

Prof. Xie's group is interested in evaluating the process, limits, and applications of monolayer dispersion of oxide catalysts. Low melting compounds (oxides, salts, complexes, organic molecule solids, etc.) can disperse spontaneously onto surfaces of supports (γ-Al_2O_3, SiO_2, C, zeolites etc.) to form monolayers or submonolayers at temperatures below their melting point (Figure C.23). The group of Prof. Xie is investigating the effect of loading on the formation of monolayers versus particles on various supports and correlating the structures to catalytic properties.

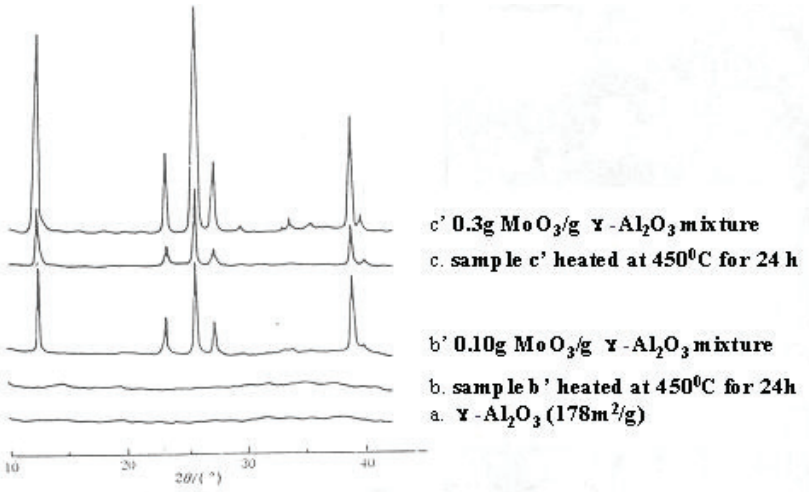

Figure C.23. XRD patterns of MoO_3 / v. Al_2O_3 system before and after heating at 450°C.

For example, a loading of 0.15 g NiO on γ-Al_2O_3 will produce monolayer dispersion, while a loading above 0.60 g will form crystalline nanoparticles. It is believed that the molecules move across the surface by diffusion and anchor onto low-energy sites when the loading is enough to form a monolayer or submonolayer. However, molecules coalesce to form large crystalline particles when the loading exceeds the threshold of one monolayer. Monolayer dispersion can also be used to alter the properties of zeolites. The structure and properties of these catalysts have been characterized using XRD, TEM, ion scattering spectroscopy, and EXAFS. Prof. Xie's group has demonstrated that the monolayer dispersion improves the catalytic properties hydrodesulphurization reaction, oligomerization of olefins, NO_x storage and reduction, etc. A high-efficiency adsorbent composed of monolayer CuCl on a zeolite that was developed to remove trace amounts of CO in H_2, N_2, and CO_2 has been patented and is currently commercialized in China. This group has also investigated the important role of trace water on the growth of single-walled carbon nanotubes on Fe/MgO catalysts.

SUMMARY/CONCLUSIONS

Catalyst research at Peking University is directed towards synthesis of nanoscale catalysts both in solid and in liquid phase. All of the PIs the WTEC team met have a high level of funding. Most catalyst synthesis, characterization, and property measurements are conducted on campus, except for the use of a synchrotron source, for which they travel to Japan (University of Science and Technology). In-house characterization facilities include XPS, GC, HRTEM, TGA, DSC, confocal Raman and IR, and mass spectrometry. Although there is not a strong component of theory and modeling, Professors Kou and Liu are using DFT calculations to describe small-size particles (50 atoms) and are modeling reactions in solution to compare with experimental results. There are some national (e.g., with Tsinghua University and the Dalian Institute of Chemical Physics) and some international collaborations with researchers at Peking University. The patent

applications are handled by the PIs, and fees are covered by their grants; therefore, most of the patent applications are submitted for China only.

The funding is mostly from government sources (Natural Science Foundation of China, Ministry of Education, and Chinese Academy of Sciences), but about 20–30% of the research is supported by industry. The catalysis groups have a very high level of success (90%) in obtaining government funding compared to the rest of China. They are also a part of large collaborative consortium of 60–70 researchers funded at a level of $20-30 million for 5 years.

Most of the graduate students are from China, but they do accept short-term visits from international students. Peking University researchers also have resources to sponsor exchange students.

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BACKGROUND

The Photon Factory was the first place the WTEC panelists visited in Japan. This synchrotron facility is extensively used by academic groups throughout the country. Several instances of applications of synchrotron radiation at the Photon Factory were observed in subsequent visits to the University of Tsukuba, University of Tokyo, AIST, and Hokkaido University.

The Photon Factory (PF) is part of the High-Energy Accelerator Research Organization (KEK), a government-sponsored research organization in Japan that supports research using particle accelerators. The Photon Factory manages two storage rings (PF and PF-AR) that combined contain approximately fifty beamlines used in a variety of X-ray, soft-X-ray, and VUV applications. The Photon Factory storage rings are by now mature technology and compete with new and third-generation synchrotron facilities in Japan and throughout the world. The facility keeps its infrastructure up-to-date by improvements in the storage rings and the addition of new beamlines (some of which are discussed below).

One of the main responsibilities of the Photon Factory is to provide the physical and intellectual infrastructure for synchrotron radiation research throughout Japan's academic community. Although the focus of the institution is fundamental research, approximately 4% of the beam time is used by industry for applied research. The ratio of industrial use comes up to about 15% in some beamlines. The KEK technical staff comprises ca 700 persons, of which 120 work in the Institute of Materials Structure Science (IMSS), the division within KEK responsible for most catalysis research. There are more than 3000 registered users of the PF, and the institute receives about 10,000 person-visits per year. The scientific staff of the IMSS provide training and technical support to users but in addition conduct their own research using synchrotron radiation individually and in collaboration with external research groups.

The Photon Factory (KEK/IMSS) allocates beamline access through competitive grants where scientific impact is the most important criterion for the ranking of research proposals. A committee reviews experimental proposals, and the Advisory Committee for IMSS formally approves the recommended proposals. General-type proposals are the most common, and these are effective for a period of two years. Between 600 and 700 proposals are active in any one year, and over 300 proposals are accepted every year. Approximately 30% of the active proposals can be classified as "Chemistry," where most catalysis applications of synchrotron radiation can be found. The PF trains new users of synchrotron radiation through workshops and seminars. The numerous PF users self-organize into user groups, usually by technique. The user groups maintain discussion websites and other activities that help train new users and that provide input to the administration of the PF about the scientific needs and future directions of synchrotron radiation. The

WTEC team found that Japan's catalysis community's largest use by far of synchrotron radiation is X-ray absorption spectroscopy. The EXAFS user group is also one of the largest user group in the PF. Structural studies of catalysts using X-ray diffraction and small-angle X-ray scattering appear to be infrequent.

CATALYSIS RESEARCH ACTIVITIES

X-ray absorption fine structure is used extensively for the characterization of catalytic materials *ex situ* and through *in situ* studies. Below we report two instances of the use of synchrotron radiation to investigate the structure and chemistry of catalytic materials.

In Situ XAFS of Ni_2P/SiO_2 Hydrodesulfurization Catalyst

This is the first XAFS measurement of HDS catalysts under catalytic reaction conditions of high pressure (3 MPa) and high temperature (613 K). This study has been possible by the development of a low-volume cell with cubic BN windows. These newly developed windows are X-ray-transparent, chemically stable, and have a very high tensile strength. EXAFS measurements on a Ni_2P/SiO_2 sample were conducted after hydrogenation at 3 MPa and under reaction conditions (using a simulated oil feed). Although the two spectra are quite similar, subtraction of the two spectra reveals the presence of Ni-S bonds. The data indicate that although the bulk of the Ni_2P nanoparticles in this catalyst remains unaltered under reaction conditions, a "skin" of partially sulfided nickel is formed (NiP_xS_y). For further details see Kawai et al. (2006).

Structure of Ni atoms on TiO_2 Determined by Polarization-Dependent Total-Reflection Fluorescence EXAFS

Identification of the adsorption site of metal species on metal oxide surfaces is a necessary step towards understanding the electronic effects of oxide supports on metal catalysts. Koike and co-workers (2006) have used the polarization-dependent total-reflection fluorescence EXAFS (PTRF-EXAFS) technique to determine the 3D surface structure of overlayers of metals interacting with substrate surfaces with Ångstrom resolution. A model system prepared by evaporation of Ni onto the TiO_2 (110) surface was investigated by obtaining EXAFS spectra along the [001], [1 –1 0] and [1 1 0] orientations. The analysis reveals that Ni atoms are located at the step edge of TiO_2 (110) surfaces. Together with results from other systems, these studies indicate that metal atoms should be located at the sites to which the dangling bonds of the surface oxygen atoms are directed.

Two new beamlines at the PF-AR promise to have much impact on catalysis research. The beamline AR-NW10A is dedicated to hard X-ray XAFS/AXS. This beamline should allow the investigation of elements that are important in catalytic applications and that are difficult to obtain in typical XAFS facilities. These include Rh XAFS and Ce K edges.

The AR-NW14A is a new beamline dedicated to time-resolved X-ray diffraction and absorption experiments. The goal of the line is to observe chemical dynamics triggered by optical pulses. Also AR-NW2A is a beamline dedicated to time-resolved XAFS experiments using tapered undulator source. Various XAFS experiments are carried out on catalytic processes; see, for example, Suzuki et al. 2003 or Suzuki, Inada, and Nomura 2006.

SUMMARY AND CONCLUSIONS

The suite of synchrotron instruments and facilities available at the PF allows Japanese investigators (and catalysis researchers in particular), including those in private companies, to conduct conventional and cutting-edge experiments. Accessibility to these facilities is widespread among the catalysis community. There are ongoing efforts to develop instruments for *in situ* characterization of catalysts (at high pressure and temperature) and for time-resolved measurements of samples under dynamic conditions.

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BACKGROUND

To help bolster Korea's self-reliance on high technology, the Pohang Iron and Steel Company established the science and technology research university known as POSTECH, the Pohang University of Science and Technology. POSTECH is home to Korea's only synchrotron radiation facility, the Pohang Light Source; Korea's largest biotechnology research center, the Postech Biotech Center; the National Center for Nanomaterials and Technology; and the intelligent robot research center, the Pohang Institute of Intelligent Robotics. The university has approximately 3,500 students, 700 researchers, and 220 faculty members.

At the undergraduate level, POSTECH has ten departments: Chemical Engineering, Chemistry, Computer Science & Engineering, Electronic & Electrical Engineering, Industrial & Management Engineering, Life Science, Material Science & Engineering, Mathematics, Mechanical Engineering, and Physics. At the graduate level, there are five departments (Mathematics, Physics, Chemistry, Chemical Engineering, and Material Sciences & Engineering); three divisions (Molecular and Life Sciences, Mechanical and Industrial Engineering, Electrical and Computer Engineering); one graduate school (School of Environmental Science & Engineering); and two specialized graduate schools (Graduate School for Information Technology, and Graduate Institute of Ferrous Technology).

Figure C.24. Pohang Light Source: 2.5 GeV Synchrotron Radiation Facility located at Postech.

RESEARCH AND DEVELOPMENT

Since the panel was unable to visit POSTECH during its travel to Asia, panel chair Davis met with Professor J.S. Lee in the Hilton Americas hotel in Houston, TX, on 18 May 2007. Both Davis and Lee were attending the North American Meeting of the Catalysis Society.

Research in energy and the environment is of great interest at POSTECH and throughout Korea. Government funding for energy research in Korea is expected to continue for at least the next decade and will likely be a major focus of activities in the near future. Although research in environmental catalysis has involved end-of-pipe technologies such as deNO_x and deSO_x reactions, more recent work has included the conversion of renewable feedstocks to chemicals. For example, the conversion of glycerol to propylene glycol, acrolein, and other products is being investigated to avoid the use of propylene for chemicals. Although there was some effort in Korea about a decade ago to recover and utilize CO_2 from combustion processes, a recent shift in direction is away from CO_2 utilization and toward energy efficiency.

Research in catalysis at POSTECH is centered mainly in Chemical Engineering. Professor J.S. Lee is currently working on photocatalysis for H_2 production. Synthesis of highly crystalline nanomaterials (i.e., Fe_2O_3, WO_3, and perovskites) with high surface area is an important component of his photocatalysis efforts (Kim et al. 2005). A second area of interest involves tungsten carbide as a fuel cell electrocatalyst component. J.S. Lee has determined that WC with a very small amount of Pt functions effectively as an electrocatalyst in a direct methanol fuel cell (Ganesan and Lee 2005). Thus, high loadings of expensive transition metals such as Pt and Ru are avoided. Professor J.S. Lee is also investigating polymer-inorganic composite membranes for the fuel cell electrolyte with a goal of reducing methanol crossover and maintaining high water content at temperatures exceeding 100°C (Rhee et al. 2005). Professor J.S. Chung is currently studying the reaction engineering aspects of solid oxide fuel cells and immobilized biocatalysts for wastewater treatment. Professor K.H. Lee is involved with catalysis for the production of fine chemicals and pharmaceuticals. For example, he is studying how Pd/carbon selectively hydrogenates –CN groups in complex molecules (Noh et al. 2004). K.H. Lee is also studying glycerol conversion to acrolein (and its subsequent oxidation to the acid) as well as screening a variety of solid acid materials. Professor I.S. Nami is investigating deNO_x catalysis for stationary and mobile sources. His work involves both hydrocarbon and urea deNO_x reactions over copper-containing zeolites, silver catalysts, and vanadium supported on titania.

Synthesis of catalytic materials is important to professors at POSTECH. Methods such as template-assisted synthesis and microwave-assisted sol-gel synthesis are used to produce a variety of inorganic oxides, sulfides, and carbides. Moreover, CVD synthesis of multiwall carbon nanotubes is also being investigated.

Catalysis research at POSTECH is supported by an impressive array of instrumentation. The catalysis labs themselves are equipped with common characterization equipment such as laboratory X-ray diffraction, IR spectroscopy, X-ray photoelectron spectroscopy, physical and chemical adsorption, thermogravimetric analysis, and UV-Vis spectroscopy. A 300 MHz magic-angle-spinning solid-state NMR facility is used routinely by catalysis researchers, especially for analysis of Al, Si, and C. The central facility at POSTECH houses advanced microscopes such as TEM, SEM, AFM, and STM. Most importantly, POSTECH is home to Korea's only synchrotron radiation source. The electron storage ring operates at 2.5 GeV with a typical current of 200 mA. Although current research involves radiation produced at bending magnet beam lines, wiggler lines are under construction. Two lines are dedicated to high-energy X-ray absorption spectroscopy (one line ranging from ~3 to 10 keV and the other from ~5 to 15 keV), and three lines are dedicated to diffraction. A small chemistry lab is associated with the beam lines; however, all analytical equipment for catalysis research is supplied by the user. According to J.S. Lee, the highest priority for new instrumentation would allow characterization of catalysts during reaction. For example, Lee would like to obtain *in situ* EXAFS during photocatalysis.

There is a minimal effort in the use of quantum mechanical calculations in catalysis research at POSTECH. Professor J.S. Lee is using the commercially available DFT software package WIEN to calculate the band positions, band gap energy, and optical absorbance of his photocatalytic materials.

Intellectual property generation at POSTECH is influenced by Korea's BK21 (Brain Korea 21st Century) program. Thus, during performance evaluations of faculty members, four patent applications count as one published paper, and two granted patents count as one paper. For Korean patents, the university covers 100% of the cost of the application, whereas for international patents, the costs are shared equally between the university and the individual's research program. If royalties are received from a patented invention, the money is shared among the inventor, the department, and POSTECH, with 40% going to the inventor. Professor J.S. Chung has started two companies based on his work with immobilized biocatalysts for wastewater treatment and with a cylindrical design of solid oxide fuel cells with heat recovery.

Each professor at POSTECH has approximately 200 m^2 for his or her individual research program; however, less space is allocated to a theory-based program. The research space has on average about 10–15 graduate students (70% PhD) and 1–2 postdoctoral researchers. Most of the students are from Korea, with a small number from China or India. Although some of the postdoctoral researchers are Korean, these scientists tend to come from China or India. Top schools in Korea such as POSTECH attempt to recruit their own high-quality undergraduates into their graduate programs. Financial support for graduate students in catalysis is mainly from the BK21 program, which pays 70% of the cost of graduate students and postdoctoral researchers in chemical engineering at POSTECH. Professor J.S. Lee indicated that funding for his laboratory is currently ~$570,000/year, from sources such as the Korean Science and Engineering Foundation (KOSEF), designation as a National Research Laboratory for Photocatalysis, General Motors, and other industrial grants. The average funding rate for other catalysis researchers is estimated to be about $300,000/year from mostly government sources. The success rate for government proposals in the catalysis area at POSTECH is estimated to be ~60–70%.

The job market for catalysis graduate students appears to be fairly strong at the moment. However, there is a mismatch in priorities between the research institutions and the companies hiring the graduates. The academic institutions are preparing students for materials, energy, and environmental research, whereas a large fraction of catalysis jobs in industry is in the more traditional chemical catalysis area. The job market is tighter for students in theory, modeling, and fundamental surface science than for those in traditional catalysis.

SUMMARY AND CONCLUSIONS

Catalysis at POSTECH is a strong research program involving at least 4 professors, all located in Chemical Engineering. The relatively applied nature of catalysis in Korea compared to the United States is consistent with most of the Korean catalysis researchers being located in Chemical Engineering. The research tends to be in the areas of energy and the environment, which is typical of other institutions in Korea as well as the rest of Asia. The programs at POSTECH are well funded by BK21 and other government and industrial sources. POSTECH is unique among Korean institutions, since it is home to the only synchrotron light source in the country. The laboratory infrastructure is apparently very good, and the job market for catalysis students graduating from the programs is fairly strong.

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BACKGROUND

The Research Institute of Petroleum Processing (RIPP) is a comprehensive petroleum refining and petrochemical science and technology research development organization for the China Petroleum & Chemical Corporation (known as "Sinopec"). RIPP is mainly devoted to the development and application of petroleum refining and integrated petrochemical technologies. In recent years, it has focused on new alternative fuel and energy sources; it also devotes much attention to basic research.

RIPP's R&D capability includes

- Crude oil evaluation
- Refining technologies
- Catalysts
- Petroleum products

Figure C.25. The RIPP Research Center.

R&D activities include clean gasoline and diesel production, heavy crude oil processing, aromatics production, lubricant production, and petrochemicals production. In addition, RIPP also engages in research on alternative fuels, basic research in oil refining technology, and technology for crude oil and product analysis.

RESEARCH AND DEVELOPMENT

RIPP is staffed with 960 people, including 782 professionals in 17 research departments. Among them are 6 members of Chinese Academy of Sciences and Chinese Academy of Engineering, 76 senior engineers with professorship, 330 senior engineers and technicians, 160 with PhD degrees, 190 with Master's degrees, and approximately 200 graduate students. RIPP is equipped with approximately 700 laboratory- and pilot-scale plants and a large array of advanced analytical equipment (300 MHz solid NMR, 500 MHz liquid NMR, mass spectrometer, FEI Company SEM with 2 nm resolution, Tecnai F20 with EDAX and GIF, XRD diffractometers, BET, IR, Raman, chemisorption, and TGA) engaged in R&D of oil refining technologies, petrochemicals, fine chemicals, additives, and petroleum product applications. RIPP has 6 scientists doing computational work; however, no details were given.

In order to meet China's newly adopted fuel standards (similar to the European standards) a new, high-activity unsupported Ni catalyst is under development for desulfurization and aromatic saturation of diesel fuels and desulfurization of fluid catalytic cracking (FCC) naphtha. RIPP also remains active in heavy oil hydroprocessing, including research on tar sands in collaboration with a group in Canada. Another large research program area is the development of zeolites and FCC technology. Additionally, RIPP has a research group on the fundamentals of zeolites and has commercialized its deep catalytic cracking (DCC) processes. A clean fuel project includes new catalysts for the production of isobutane and propylene (for alkylation) by FCC. RIPP has also developed some high-performance lubrication oils for space and military applications, a process for ethylbenzene (EB) from FCC off-gas (benzene plus ethylene alkylation), and a methanol to olefins process. Additionally, RIPP is currently developing a magnetically stabilized fluid bed reactor that has been scaled to intermediate size (6 m x 18 m). The specific application was not disclosed. RIPP representatives indicated that they are able to fluidize even alumina particles. RIPP is also developing a 50,000 tons/year demonstration plant for production of biodiesel by methanol esterification of palm oil obtained from Indonesia. The reaction is done in supercritical methanol without catalyst, since contaminants in the oil foul traditional catalysts. Currently, there are no projects on cellulose processing or CO_2 reactions.

SUMMARY AND CONCLUSIONS

RIPP has a comprehensive refining R&D program in petroleum and petrochemical research with strengths in hydroprocessing and zeolite catalyst processes. The analytical department has a large variety of state-of-the-art commercial equipment for catalyst and hydrocarbon analysis. Currently, there are no *in situ* catalyst characterization studies. Research projects are market-driven, and RIPP has an effective program to move developments from the lab to demonstration and commercial scale.

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BACKGROUND

Seoul National University was established in 1946 as the Republic of Korea's first national university; it included the Colleges of Agriculture, Commerce, Dentistry, Education, Engineering, Arts, Law, Liberal Arts & Sciences, and Medicine, and a Graduate Division. The University has since grown to 16 Colleges, 1 Graduate School, and 6 Professional Schools with a total enrollment of 19,208 undergraduates and 10,088 graduate students that are served by 2,188 full-time faculty members and 1,947 staff members. The University is quite selective, with a 19% acceptance rate for undergraduate applicants (2005) and an average score on the National Entrance Exam of enrolled freshmen in the top 2.5%. The high number of research articles published by faculty in journals recognized by the Science Citation Index (2005) places Seoul National University in the top thirty in the world. The university is proud of its broad alumni base in very high-ranking positions in public service, law, business, and academia.

The Department of Chemical and Biological Engineering is home to most of the research in catalysis by nanostructured materials. Of the 32 faculty members in the department, 5 are involved in catalysis. The total number of graduate students in catalysis research is about 50-60, split evenly between MS and PhD students. While there is some catalysis activity in the Department of Chemistry, the focus in that department is on homogeneous and enzyme catalysis.

Funding for catalysis is obtained mostly from government sources. The Chemical and Biological Engineering Department participates in the BK21 program (Brain Korea 21st Century), which supports the majority of costs of graduate students. The department also has funding to support six National Research Laboratories (5 years), a Creative Research Initiative (9 years), and an Engineering Research Center. Funding from oil companies and Samsung is estimated to contribute about 20–30% of the external research support.

RESEARCH AND DEVELOPMENT

During its visit to Seoul National University, the WTEC panel met with five faculty members of the Chemical and Biological Engineering Department and toured some of the labs. Brief descriptions of the research activities are given below.

Professor Sang Heup Moon focuses on three main topics in his group at the Surface Engineering Laboratory (http://surf.snu.ac.kr/homepage/eng2.htm). The first topic involves the search for appropriate promoters and methods to deposit promoters on Pd/SiO_2 catalysts for the selective hydrogenation of acetylene to ethylene. The second area of interest involves the synthesis of highly dispersed CoMoS hydrodesulfurization catalysts that have been modified by acidic additives. The third topic involves the study of Pt/carbon electrocatalysts with Cr and Si promoters for use in fuel cells. Professor Moon makes extensive use of temperature programmed reactions and IR spectroscopy in his lab. Although electron microscopy is available in a central facility for materials characterization, a new HRTEM would help speed the analysis of catalyst samples on the campus.

Professor Ho-In Lee is interested in depositing onto supports controlled particle sizes of metals prepared in solution. In particular, Professor Lee is studying the application of Pt nanoparticles as electrocatalysts for polymer electrolyte membrane fuel cells that run on hydrogen or methanol. Professor Lee is also involved in work on molten carbonate fuel cells for conversion of methane to electrical power. In this case, the methane is reformed internally in the anode chamber of the cell. The electrocatalysts of interest in this system are Ni particles supported on $MgTiO_x$ and $MgSiO_x$ and are designed to function at the high temperature (~650°C) of a molten carbonate fuel cell. The goal is to create a stable electrocatalyst that is resistant to poisoning by the electrolyte.

Professor Taeghwan Hyeon, the Director of the National Creative Research Initiative Center for Oxide Nanocrystalline Materials (see http://nanomat.snu.ac.kr/research.htm), is focused on the synthesis of uniform nanoparticles. The key synthetic method in this state-of-the-art approach involves thermolysis of metal-surfactant complexes. This group has been able to successfully synthesize monodisperse spherical nanocrystals of Fe, Co, magnetite, cobalt ferrite, Ni, MnO, Pd, zirconia, ceria, and Au. The group has also produced monodisperse phosphides and sulfides, as illustrated in Figure C.26. By using silica nanostructures as templates, Prof. Hyeon has successfully produced nanostructured carbon materials for use as adsorbents and supercapacitors. Most recently, Professor Hyeon has been studying the synthesis of MnO nanoparticles for use as magnetic resonance imaging contrast agents; this work is carried out in collaboration with the Samsung Medical Center. The major analytical instruments in Professor Hyeon's lab are an X-ray diffractometer and a JEOL 2010 transmission electron microscope. Professor Hyeon indicated a desire for improved access to synchrotron radiation to help elucidate the synthesis mechanisms.

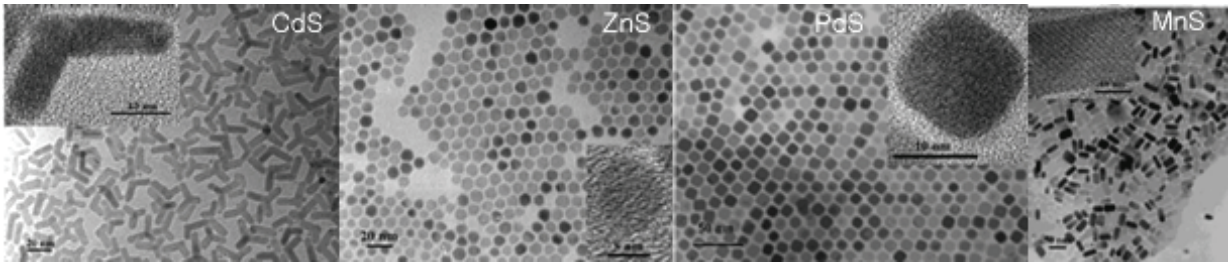

Figure C.26. Electron micrographs of uniform nanocrystalline sulfides prepared in the group of Prof. Hyeon (from http://nanomat.snu.ac.kr/research.htm).

Professor In Kyu Song's group at the Molecular Catalysis & Reaction Engineering Laboratory investigates a very wide array of catalytic reactions with an industrial orientation. In particular, his website http://catalysis.snu.ac.kr/ indicates an interest in developing molecular catalysts for the following reacting systems:

1. Synthesis of dimethyl carbonate from methanol and carbon dioxide
2. Ziegler-Natta/metallocene hybrid catalyst for LLDPE production
3. Hydrogen production for fuel cell by auto-thermal reforming of ethanol
4. Hydrogen production for fuel cell by steam reforming of LNG
5. Synthesis of dichloropropanol from glycerol
6. Oxidative dehydrogenation of n-butene to 1,3-butadiene
7. Hydrogen storage and recovery
8. Epoxidation of propylene into propylene oxide
9. Middle distillate production by hybrid Fischer-Tropsch catalyst

A major component of Prof. Song's program involves the synthesis, characterization, and catalytic activity of supported polyoxometalate monolayers, as studied by scanning tunneling microscopy.

Professor J. Yi's group at the Environmental Materials and Process Laboratory (http://empl.snu.ac.kr/empl-new/html/index2.htm) combines principles from chemical engineering, nanotechnology, and environmental technology in his research. Prof. Yi utilizes the tools of nanotechnology such as scanning probe lithography to fabricate catalysts and other nanodevices. The applications of his nanostructured systems include novel catalysts for wastewater treatment by wet oxidation, new fuel cell electrocatalysts, materials for hydrogen storage, visible light activated photocatalysts, Au nanoparticle sensors, and Au catalysts.

SUMMARY AND CONCLUSIONS

Seoul National University is a world-class research university with significant activities in catalysis. Although the overall focus of the catalysis research is applied in nature, novel nanomaterials synthesis work is being performed at the institution by several investigators. At this point in time, there is very little activity in theory and modeling in catalysis. The physical infrastructure and characterization facilities are very good. and the financial support for catalysis research is impressive. The Department (School) of Chemical and Biological Engineering participates in the BK21 program that funds graduate education and has an Engineering Research Center for Energy Conversion and Storage and the National Creative Research Center for Oxide Nanocrystalline Materials.

Site: **Tianjin University**
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http://202.113.13.66/eweb/index.htm

Date Visited: The WTEC team did not visit Tianjin University in person but rather met with key professors at the Jade Palace Hotel, Beijing, on June 4, 2007.

WTEC Attendees: J. T. Miller (report author), R. J. Davis, R. Sharma, and G. Hane

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BACKGROUND

Tianjin University was founded in 1895 and is billed as "the first institution of higher learning in modern China." It is a "National Key University" directly under the administration of the Ministry of Education of China. It has 18 academic schools, 51 undergraduate programs, 154 Master's programs, and 92 Doctoral programs. Among these are 22 so-called "State Key Research Disciplines." There are also 3 State Key Laboratories on the campus and 1 State Engineering Research Center. The combined student population is 26,000, and there are 4400 faculty and staff. Its Chemical Engineering School was strengthened in the beginning of the 1950s with the government-forced relocation of the most successful chemical engineering professors in north China and with the help and involvement of the former USSR. The global chemical engineering and technology program in the school was ranked two times as first in China. The ranking was organized by an agency under the Ministry of Education of China and was carried out in 2003 and 2007.

Tianjin Key Laboratory of Applied Catalysis

The Tianjin Key Laboratory of Applied Catalysis is supported by Tianjin Municipal Government and is organized by the Department of Catalysis Science and Technology in the School of Chemical Engineering and Technology of Tianjin University. The lab has 12 staff members, 8 faculty members, and 1 visiting professor. Its industrial catalysis program has twice been ranked as the best in China, in 2001 and 2006.

Research Areas

- Catalysis and reactor engineering (general)
- Environmental catalytic technologies
- Catalytic membrane reactors and other reaction-separation technologies
- Photo-stimulated catalytic reactions
- Sustainable technologies and green processing

- Hydrocarbon conversion and hydrogen energy systems
- Particle technology and multiphase processing

Key Laboratory of Green Chemical Technology of the Ministry of Education

This Laboratory has 45 faculty, 70 MS students, and 20 PhD students.

Research Areas

- C1 chemistry and technology
- Organic chemical technologies based on petroleum and coal
- Bio-ethanol
- Environmental catalysis
- DFT studies
- Advanced chemical technologies

RESEARCH AND DEVELOPMENT

Professor Li's research at the Laboratory of Applied Catalysis is focused on the development of fuel cell energy system, including carbon fuel cells, for new and clean energy. While thermal efficiencies of gasoline and diesel cars, power generation, etc. are from 15–40% and PEM fuel cells are about 55%, carbon fuel cell efficiencies are higher, at about 80%. In addition, the fuel requirements for the fuel cell are less demanding. Figure C.27 gives a conceptual schematic of an efficient energy conversion process based on a methane decomposition reactor, a PEM fuel cell and a carbon fuel cell. Professor Li's calculation shows the system is highly efficient.

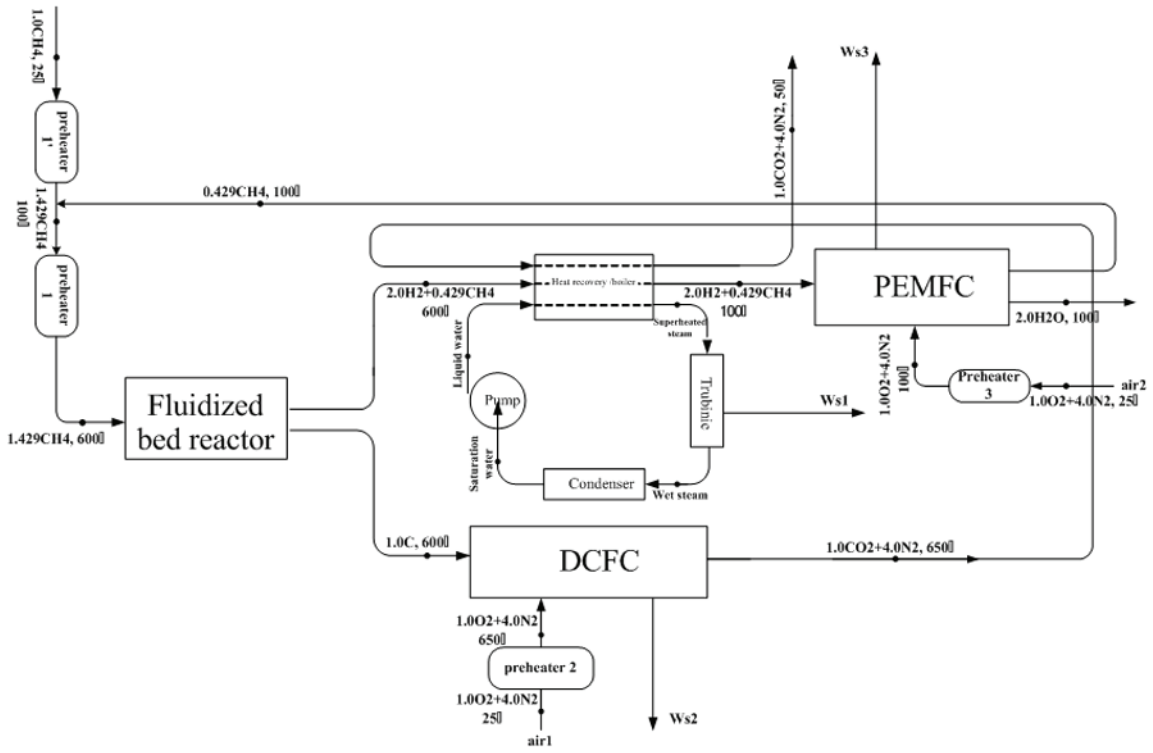

Figure C.27. Scheme of highly efficient energy conversion process based on natural gas decomposition reactor, carbon fuel cell, and hydrogen fuel cell (courtesy of Prof. Li; from the keynote lecture of the Green Chemical Technology Conference, 2006, Tianjin).

Professor Li's group is also working to reduce the energy and capital investment for hydrogen production for PEM fuel cells. Research teams are developing ion-conducting membranes for air separation and hydrogen production by combining reaction and separation in a membrane-WGS reactor. Membranes under development include carbon nanotubes grown on porous alumina (Figure C.28) and modified stable Pd alloy membrane. They recently developed a composite electrolyte membrane with very fast ionic conduction for intermediate-temperature ceramic fuel cells.

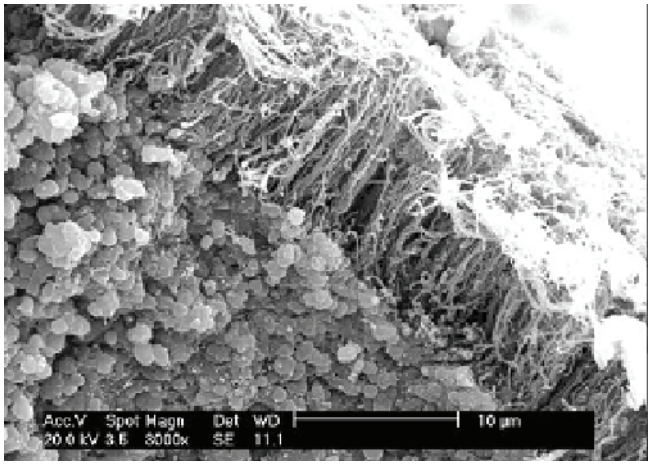

Figure C.28. SEM micrograph of fibrous carbon nanotubes grown on porous alumina (circular particles).

Professor Li also has an extensive program for the characterization and optimization of the mechanical properties of catalysts. The mechanical properties of greatest interest are those of macroscale reliability of reactors and correlations; however, Li's group also has made great effort to find the relationships between macro- to micro- and nanoscale parameters. Test methods and design equations are developed to measure changes in physical properties due to thermal, chemical, and mechanical stress during commercial use. The group has applied these methods to develop commercially robust catalysts for industry. It has also examined the mechanical properties of structured alloy and ceramic catalyst support. A review article on this topic was published in AIChE Journal (Wu, Zhou, and Li 2007).

Professor Liu's group at the Key Laboratory for Green Chemical Technology of the Ministry of Education includes the utilization of cold plasmas for activation of C1 molecules and for catalyst preparation. The group has confirmed that the argon or air glow discharge plasma can be applied for reduction of metal ions with the positive standard electrode potentials (like noble metal ions). The plasma reduction operation is simple and easy. The energy consumption and the material cost for the plasma approach are around 40% and 1% as little as those for the hydrogen reduction method, according to laboratory scale tests. The plasma reduced Pd and Pt catalysts have showed excellent activity for hydrogen storage (in cooperation with Prof. Ralph Yang at University of Michigan), fuel cells, glucose oxidation and CO_2 reforming. The electrons within the cold plasmas were considered as the reducing agents for the reduction of metal ions.

Professor Liu's group is also working on the plasma decomposition of metal precursors for catalyst preparation. A typical example is the preparation of Ni catalysts for CO_2 reforming. The Ni based catalysts show very good activity for methane reforming but tend to be deactivated due to the serious coke formation. The glow discharge plasma treatment of Ni catalysts followed by calcinations and reduction thermally leads to a significant improvement in the coke resistance. Such plasma treated catalyst contains high concentration of close packed plane with improved Ni dispersion and enhanced Ni-alumina interaction, which lead to high catalytic activity and excellent resistance to formations of filamentous carbon and encapsulating carbon.

Figure C.29 shows a low-temperature plasma used to reduce metal catalysts. The catalyst sample is placed in a quartz tube and treated with flowing Ar glow discharge plasma. Plasma reduction produces metallic particles with different morphologies and reactivity.

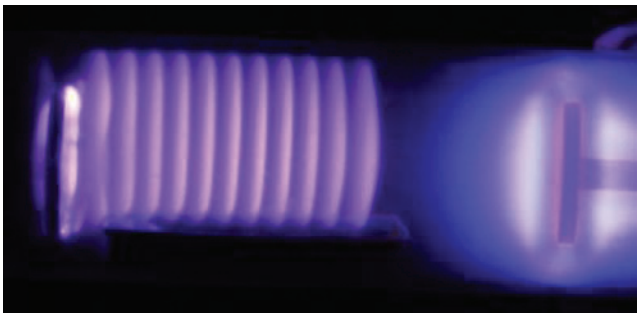

Figure C.29. Glow discharge with catalyst.

SUMMARY AND CONCLUSIONS

A central theme of research activities in China is the production of clean energy for the growing economy. Utilization of natural gas, i.e., methane, is challenging, but its usage is expected to continue to grow. While technically very challenging, fuel cells are more efficient than current energy technologies, and carbon fuel cells have even greater potential if a workable process can be developed. Professor Li is working to simplify hydrogen production for PEM fuel cells by combining reaction and separation, and he is working on the fluid bed reactor to decompose natural gas into H_2 and C for a carbon fuel cell process. Professor Liu is working on activation of C1 molecules for the production of chemicals and fuels. He is also working on catalyst preparation using cold plasmas. The nucleation and growth of the metal particles under the influence of cold plasmas are different from the conventional approaches. Catalysts with specific performance can be made this way. A new plasma catalyst reduction methodology is being also developed.

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Date Visited: June 8, 2007

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Hosts: Prof. Takashi Tatsumi
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Dr. Junko Kondo
Dr. Satoshi Inagaki
Dr. Toshiyuki Yokoi

BACKGROUND

The Tokyo Institute of Technology is one of the premier graduate research institutions in Japan. It has close to 5000 undergraduate students, over 3000 students in the Master's program, and 1500 doctoral students. Three groups work in catalytic chemistry: the group of Prof. Tatsumi (heterogeneous catalysis), the group of Prof. Iwamoto (mesoporous materials and materials science), and the group of Prof. Baba (catalysis and reaction engineering).

Prof. Tatsumi is supported by one associate professor (Dr. Junko Kondo) and two assistant professors (Dr. Satoshi Inagaki and Dr. Toshiyuki Yokoi). We had the opportunity to briefly interview all of them. Currently, the laboratory has four postdoctoral fellows (from China and Taiwan), four PhD students, and six MS students (one of these from Italy). Funding for supporting postdoctoral fellows and students comes both from government and industry.

The laboratory resources for catalysis research are excellent. These include catalyst synthesis facilities (by mainly hydrothermal methods), catalyst characterization (by physisorption and chemisorption), several *in situ* IR spectroscopy units, various reactors equipped with gas chromatographs, X-ray diffraction instruments, scanning and electron microscopes, one 400 MHz solid-state NMR spectrometer, and other units.

CATALYSIS RESEARCH ACTIVITIES

The research in Tatsumi's group can be classified as "green chemistry" with an emphasis on zeolite synthesis and catalysis. One aspect of the research is the development of new acid catalysts through the synthesis of new materials. An example of this research effort is the synthesis of zeolite MCM-22 (MWW) containing titanium atoms in the framework (Wu et al. 2001) that has been investigated extensively by the group for epoxidation of alkenes using hydrogen peroxide as the source of oxygen. More recently, the group also reported a layered precursor to the Ti-containing MCM-22 zeolite. This material shows promising catalytic properties because it has activity similar to the one observed in TS-1 titanosilicates, but it is particularly active for bulky cycloalkenes, molecules that are excluded from the TS-1 pores by molecular sieving effects (Fan et al. 2006). At this time, work continues to determine why the post-synthesis treated Ti-MWW is a better catalyst than the materials that have not been treated.

Another example of a new material with interesting catalytic properties is organic-inorganic hybrid zeolites containing organic frameworks (Yamamoto et al. 2003). These materials, developed in the Tatsumi laboratory, contain Si-CH_2-Si groups instead of the typical Si-O-Si groups present in the zeolite structure. These groups allow for shape-selective lipophilicity that can be used to advantage in several chemical transformations such as esterifications.

The research of Prof. Tatsumi is directed towards two primary objectives. The first and current target is the use of H_2O_2 as an oxidant for partial oxidation of hydrocarbons, with the intention of using molecular oxygen directly in the future. An example of the chemistry of interest in this group is the synthesis of PO in the Sumitomo process. The group wishes to accomplish the same reaction without using the hydroperoxide intermediate (Figure C.30), which can be prepared at low conversions at high selectivity but is potentially explosive. More attractive is the direct synthesis of PO using oxygen and hydrogen in a process analogous to the gold catalyst of Haruta (Haruta 2002). This catalyst, however, is neither stable nor active enough. The Tatsumi group is investigating various possibilities to produce the same result using novel materials.

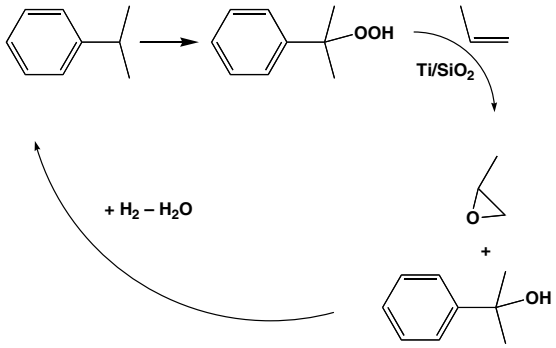

Figure C.30. Epoxidation of propylene using hydroperoxides.

The second target identified by Prof. Tatsumi is the synthesis of propylene from ethylene and methanol:

$$C_2H_4 + CH_3OH \longrightarrow C_3H_6 + H_2O$$

This reaction is highly desirable, as currently the production of propylene is tied to what is produced in fluidized cracking catalytic units, and consumption is growing substantially. The production of propylene in refineries is reaching its practical maximum and there are no clear technologies yet that can produce the additional amounts of propylene that will be needed in the future. For this reason, chemistries are needed now that will be able to alleviate the expected demand of propylene. The goal of the Tatsumi group is to develop a method for producing propylene from ethylene, which is easier to manufacture from ethane and hydrocarbons, using steam-cracking.

In the laboratory of Prof. Tatsumi, Prof. J.N. Kondo is pursuing mechanistic studies of catalytic reactions using IR spectroscopy of adsorbed molecules. For instance, she and collaborators have determined that at low temperatures, the double bond shift in 1-butene to 2-butene reaction occurs though an intermolecular path that does not involve the acid proton on the zeolite wall (Kondo and Domen 2003). Prof. Kondo was also able to establish that in the dehydration of ethanol on the acid sites of zeolites, a key intermediate is the ethoxy group. This is the first unambiguous evidence of alkoxy intermediates in dehydration reactions of C2 and larger alcohols (Kondo et al. 2005). Finally, Kondo and coworkers have conducted the first time-resolved IR study of the interaction of an alkene with a zeolite acid site. Using the two-color pump-probe technique, they were able to establish the presence of a short-lived intermediate in the reaction between acidic groups and alkenes in zeolite pores.

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BACKGROUND

A catalysis laboratory at the Tokyo Metropolitan University is lead by Professor Masatake Haruta and has one full professor, one associate professor, one assistant professor, 3 postdoctoral fellows, and 17 students (1 PhD, 10 Masters', and 6 undergraduate students). Professor Haruta has had a distinguished career, first working at the National Institute of Advanced Industrial Science and Technology (AIST) and then moving to the Tokyo Metropolitan University in 2005. The predominant focus of the Haruta catalysis laboratory is on the synthesis and application of nanosized Au catalysts for green sustainable chemistry. Professor Haruta was the first to demonstrate that nanometer-sized supported Au particles were highly active for low temperature CO oxidation in a landmark paper that was published in 1987 (Haruta et al. 1987). Since that time, there has been an exponential increase in the number of papers on the unique catalytic properties of nanometer-sized Au catalysts. In 2005 alone there were over 700 new papers published on the catalytic properties of gold for a broad range of chemical reactions.

RESEARCH AND DEVELOPMENT

The recent work by the Haruta group has shown that active Au catalysts are comprised of nanometer-sized particles of Au that are bound to a reducible oxide supports such as TiO_2, MnO_2, Fe_2O_3, Co_3O_4, NiO, or CeO_2. The junction periphery between the Au cluster and the oxide support is critical not only for anchoring the metal to support but for aiding the catalytic reaction. Both hydroxyl intermediates and water have been shown to significantly enhance the catalytic activity of Au under different conditions. The group has identified three important factors that control the activity: (1) the strength of the interaction between Au and the support, (2) the type of support, and (3) the size of the particles that form. There is strong evidence in the literature that supports these ideas as well.

The Haruta group has demonstrated that nanometer-sized particles of Au on different supports are very active and highly selective for a wide range of catalytic reactions, including CO oxidation, water gas shift, propylene epoxidation, and a number of others. In a recent study with colleagues from AIST, the group showed that Au supported on CeO_2 was much more active for the water gas shift reaction than conventional supported Cu/ZnO catalysts. The selectivity for this reaction was essential by 100% to CO_2, with no production of methane for temperatures up to 623 K. High-resolution TEM and ADF-STEM characterization was carried out to examine the size of the particles formed and the nature of the interaction of the Au

particles with the support. Figure 6.14 shows images obtained from TEM and ADF-STEM taken at 400,000x magnification.

The current work in the Tokyo Metropolitan University is focused on the use of supported Au to carry out propylene epoxidation. They have shown significant support effects for Au catalyzed propylene epoxidation when carried out over TiO_2 anatase, Ti-MCM41, Ti-β, TS-1, and TS-2. The use of TiO_2 rutile as well as amorphous TiO_2, however, leads to the production of acetone and CO_2. The selective Au clusters are shown to be 2-4 nanometers. The lab is currently synthesizing and using various base promoters such as $Ba(NO_3)_2$ and $(CH_3)_3N$ to help slow down catalyst deactivation and improve propylene oxide yields. The promoters help to suppress the combustion of H_2 and the successive oxidation of PO.

A second area of focus for this group is in the area of selective liquid phase oxidation of polyols such as glucose to gluconic acid. They have developed a range of different catalysts comprised of nm particles of Au supported on activated carbon, polymers, and oxides that are very highly active. The work has subsequently lead to pilot plant studies by Nippon Shokubai Co., which has used Au supported on silica to carry out the oxidation of ethylene glycol with methanol to produce nearly 2 $x10^4$ tons/year of methyl ester glycolate.

The group demonstrates a strong focus and expertise in the synthesis of novel materials. Professor Ishida is working on the development of Au on polymer supports where the functionality of the support that can be used to anchor the metal, control its size, and in addition provide a perimeter environment that helps to enhance the reactivity of Au. Professor Takei's group is working on the deposition of Au nanoparticles onto model metal oxide supports as well as on carbon supports in order to also create unique perimeter environments that help to catalyze oxidation of CO, HCHO and propylene.

The work of the Haruta laboratory is supported by larger collaborative research proposals such as the CREST (Core Research for Evolutional Science and Technology) grant from the Japan Science and Technology Agency. The supported work has the title "Catalyst Design of Au Clusters through Junction Effects with Metal Oxides, Carbons and Polymers" along with 10 other research groups for over ¥392,000,000. This group is lead by Professor Haruta. In addition, the group has support from the Ministry of Education, Culture, Sports, Science, and Technology Priority Area on Catalysis of Au Clusters Fixed to Nanospaced Metal Complexes at ¥18,200,000, as well as from a number of other joint research programs. The Catalysis Center is just beginning to collaborate with theoreticians at AIST Kansai and Osaka University. Nearly 80–90% of its support is derived from the government, whereas 10–20 % is from industry.

CONCLUSIONS

A catalysis laboratory at Tokyo Metropolitan University was established by Professor Haruta in 2005. The group is small but is one of the leaders in the synthesis and application of nanometer Au particles on novel supports in catalysis for green chemistry. It has a strong program in elucidating the influence of Au particle size and morphology, support interactions, and the perimeter interface in order to control of different catalytic reactions. This group is driving various major efforts in Japan that connect some of the top research laboratories in the design of novel supported Au catalysts.

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BACKGROUND

Toyota was founded by Sakichi Toyoda who first invented the Toyoda Automatic Loom in 1924 and manufactured the Toyoda Model AA Sedan in 1936. The Toyota Motor Company and Toyota Motor Corporation were subsequently established in 1937 and 1982, respectively. Toyota is currently one of the leading automotive manufacturing companies in the world. In 2006, Toyota produced over 8 million cars, resulting in net sales of ¥10,191.8 billion. The company currently employs over 65,000 people and has 15 domestic plants and 52 companies in over 26 different countries (Toyota 2007c).

Toyota's central focus is on "Innovation into the Future." One of its key goals is to be a "Good Corporate Citizen," thus to provide "…clean and safe products to enhance the quality of life everywhere…"(Toyota 2007c). The company has a very strong commitment to safety and protecting the environment, with the serious goal of achieving zero emissions. To that end, it has an impressive research effort in catalysis for clean and energy-efficient automobiles.

Research and Development at Toyota is organized along a grid of basic R&D systems, which include Basic Research and Development, Advanced Engineering Development, and Product Development systems that intersect the Basic Components, Systems, and Vehicles R&D systems (Toyota 2007a). Most of the R&D involving catalysis is carried out in the Vehicles Engineering Group under the Division of Material Engineering III (MED3), which is responsible for advanced research in vehicle development through

advanced analytical technology. The focus research areas of MED3 are advanced analytical technology, bio-resource materials, and fundamental materials for fuel cells, hybrid vehicles, and exhaust control systems.

Catalysis is an important partner across many of the focus areas in MED3, including basic analytical methods and testing, material properties, material design, and development for devices (including automotive exhaust catalysts, sensors, and fuel cell materials). There is a strong internal effort aimed at understanding the basic fundamentals of how catalysts work, developing new automotive catalysts and processes that can operate over the lifetime of the vehicle, and reducing the amount of precious metal used. Toyota presents a strong commitment to catalysis R&D, with significant efforts at the Higashi-Fuji Technical Center as well as the company's other research centers. In addition, the company collaborates and supports a broad range of catalysis activities with a number of academic groups throughout Japan as well as in the international community.

RESEARCH AND DEVELOPMENT

The predominant catalysis research efforts at Toyota span a range of different areas, including (1) three-way catalysts, (2) NO_x storage and reduction materials, (3) hydrocarbon and particulate combustion catalysts and processes, (4) PEM fuel cell catalysts and devices, and (5) automotive catalysts for emissions resulting from the combustion of biofuels.

Durability is a central and cross-cutting concern in all of these areas. The company's greatest catalysis efforts appear to be focused on the development of automotive exhaust catalysts that reduce all emissions (NO_x, CO, hydrocarbons, and particulate matter) and last the lifetime of the automobile. Furthermore there are significant efforts aimed at reducing or replacing the noble metals that are currently used as catalysts for automotive emissions. Toyota researchers place a strong focus on understanding the basic catalytic phenomena together with the intrinsic material properties as the best way to rationally develop durable catalytic materials and processes that last the full lifetime of the vehicle. This presents an interesting difference to that of many chemical companies whose focus tends to be on catalytic activity and selectivity.

Toyota's actions clearly show the company's commitment to fundamental research. In 2004 it constructed a state-of-the-art ultra-high-vacuum laboratory at the Higashi-Fuji Central Research facility where its researchers can soft-land size-selected metal clusters onto different supports in a highly controlled manner with full spectroscopic characterization. The materials are then directly transferred to a reaction chamber that can probe chemistry at more realistic catalytic conditions. There are very few facilities in the world that can carry out such fundamental studies. The lab is set up to synthesize and test the properties along with the reactivity of new nanoscale catalytic materials under near *in situ* conditions.

In addition to this cluster laboratory, the Higashi-Fuji Technical Center has outstanding catalyst and materials' characterization facilities; these include XRD, SAXS, TEM-EDX, SEM, TPD, IR, CO Plus, NMR, Raman, XPS, AFM, and STM as well as *in situ* XAFS, XRD, and TEM. It also has a number of more traditional catalytic testing units to determine kinetics and catalytic performance. Toyota is one of the few companies in the world that has TAP (Temporal Analysis of Products) reactor system, which is used to carry very short (millisecond) surface reactions to examine the surface chemistry and kinetics (Sakamoto et al. 2007). This is an important tool that has allowed its researchers to examine the transient elementary process involved in the storage, release, and reduction of NO_x over supported Pt catalysts. Fast millisecond injections along with time-of-flight mass spectrometry are combined in this work to follow the transient changes involved in NO_x release and reduction. While the WTEC panel learned of very strong efforts aimed at characterization and monitoring catalytic reactions, there appeared to be no internal efforts in the application of theory.

In the panel's visit, Toyota research leaders presented representative results for three different catalytic systems where they demonstrated how fundamental knowledge about the elementary kinetic processes obtained through careful analytical characterization of working catalytic state provided new insights into the design of more durable catalysts and processes in automotive emission catalysis. The examples included

1. the nature of the metal support interactions for three way catalysts and its influence on sintering
2. the mechanisms which control NO_x storage and reduction
3. new catalyst technology for diesel engines.

In the first system, Toyota researchers combined X-ray absorption analysis, particle size analysis from XRD and TEM, along with catalyst aging studies to understand the mechanisms and structural factors that control metal particle sintering. The three-way automotive catalyst is comprised of the precious metals (Pt and Rh), an oxygen storage component (ceria or Ce-Zr-Y [CZY] mixed oxide) and the metal support (Al_2O_3). Using TEM, they were able to follow the changes in particle size after aging tests carried out at 800°C and in an oxidizing environment. They demonstrated significant sintering for Pt supported on alumina whereby 1 nm particles coalesced into 25 nm particles (see Figure 6.16A) and essentially no sintering for Pt bound to CZY (see Figure 6.16B).

XANES and EXAFS studies were used to establish the electronic state of Pt and its local structure respectively *in situ*. The results show that the Pt bound to Al_2O_3 is Pt(0), whereas the Pt on CZY is highly oxidized. They conclude that the Pt(0) is weakly held to theAl_2O_3 surface and thus agglomerates to form larger Pt particles under oxidizing conditions. The Pt on CZY was strongly held to the oxide under aggressive oxidizing conditions thus preventing sintering.

They showed that under reducing conditions, the Pt for both systems was reduced to active Pt(0). Their findings suggest that sintering is controlled by the nature of the metal-support interaction. To prove this, they carried out further studies on Pt supported over a series of different oxides. They used XPS spectroscopy to determine the binding energy of the O(1s) electron as a measure of the electron density of oxygen in the support. They demonstrated a direct relationship between the oxygen binding energy, the oxidation state on Pt, and the Pt particle size after sintering, as is shown in Figure C.31.

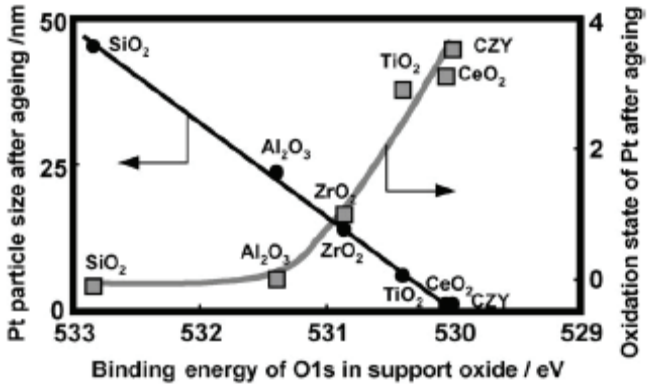

Figure C.31. The correlation between the oxygen binding energy as measured by XPS, the oxidation state of Pt determined by XAFS, and the Pt particle size after aging (Nagai et al. 2006).

In addition, the group at Toyota has made a number of advances in elucidating the fundamental mechanisms that govern NO_x storage and reduction catalysis providing solutions to a number of these issues. In order to understand this system in more detail, they deposited thin films of Ba onto an ideal Pt(111) substrate and subsequently oxidized the Ba to from BaO/BaO_2 which was then reacted with O_2 and NO to form $Ba(NO_3)_2$.Their results suggest that the mechanism may proceed by the dissociation of oxygen on the Pt step edge to form BaO at the step and BaO_2 on the terrace sites. This is shown in Figure 6.17, which is the result of STM studies of the surface carried out by Professor Michael Bowker at Cardiff University in collaboration with researchers at Toyota. NO and O_2 subsequently react with BaO_2 on the terrace forming O-Ba-NO_2. The adsorbed NO_2 can then migrate back to the step where it reacts with additional oxygen and BaO to form $Ba(NO_3)_2$. The adsorbed NO_2 species that forms is thought to be a critical intermediate in NO_x reduction.

Other fundamental research efforts on NO_x storage have helped them to overcome issues related to sulfur poisoning as well as thermal degradation. They have shown the following order for reducing agents and their ability to regenerate NO_x storage sites: $H_2 > CO > C_3H_6$. The water gas shift reaction was found to be active in reducing Pt than steam reforming.

The last system the panel's hosts presented on novel catalytic technology for diesel engines was quite impressive. They combined the results from fundamental research efforts in catalysis and engineering to develop the Diesel Particulate NO_x Reduction (DPNR) system, a new process for clean diesel technology. The DPNR system combines a novel NO_x storage and reduction (NSR) catalyst, which is coated onto the walls of a monolithic oxide particulate filter substrate, thus producing a novel material used to construct very compact size converters that reduce NO_x, particulate matter and unburned hydrocarbons simultaneously. The particulate material is trapped in this system at the inlet of the filter. The filter is coated with a NO_x storage and reduction catalyst that aids in the oxidation of PM, as there is spillover of active oxygen from the NSR catalyst under lean conditions, which helps to lower the inlet temperature required for the combustion of the PM by over 100°C.

This novel catalytic process is coupled with precise injection timing to control the amount of exhaust gas recirculation and cooling to control the temperature. Multiple fuel injections and engine management are used to precisely control the NO_x reduction and the oxidative removal of PM and hydrocarbons. The DPNR is a maintenance-free process that operates without the need for fuel additives. It relies on the sophisticated sensors that monitor the air/fuel ratio, the pressure, and the temperature but do not require expensive NO_x sensors. The precise fuel injection air/fuel ratios are critical. In this novel catalytic system, active oxygen species that are formed from the NSR catalyst are used to oxidize the particulate matter at low temperatures. This helps to ensure an appropriate temperature window for the PM/NO_x storage system, even for "cold" exhausts. The smoke from this system is considerably reduced as the combustion temperature is kept lower than that where soot formation occurs. A fuel rich stream is injected downstream in the exhaust in order to reduce the NO_x that is stored. The system was introduced in Toyota's Clean Diesel Technology in 2003

SUMMARY AND CONCLUSIONS

The catalysis program at Toyota is quite strong. It integrates fundamental science together with creative engineering in order to advance catalytic technology. The company places a high value on understanding the basic science in order to elucidate the atomic structure and the properties of different catalytic materials along with the fundamental mechanisms that govern catalysis. Its researchers believe that this is the best way to develop active yet stable materials that can last the lifetime of the vehicle. Their efforts are primarily centered on the development of advanced materials and processes for (1) three-way catalytic converters, (2) NO_x storage and reduction systems, and (3) fuel cell catalysis. These processes are critical to improving emissions and energy considerations. Their fundamental efforts have provided unique insights into the processes that control metal sintering, NO storage and reduction, particulate combustion, as well as a host of other important problems. This has led to the development of novel materials and processes that begin to overcome these issues. The Toyota Higashi-Fuji Technical Center has state-of-the-art characterization and testing facilities. In addition to the strong expertise within the company, its researchers have also partnered with a number of different researchers across Japan and throughout the world to further enhance their capabilities.

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Prof. Duan Weng
Department of Materials Science and Engineering

Approximately 10 other graduate students and postdoctoral fellows also attended.

BACKGROUND

Tsinghua University, one of the most prestigious science and engineering universities in China, was established in 1911. It is one of China's 100 universities receiving a boost in national financial support since 1993 as part of the "211" and "985" projects to build world-class educational quality and effectiveness in the 21st century. The university currently has 54 departments distributed in 13 schools; 19 institutes and research centers; and 16 national-level research centers, institutes, and "key" laboratories, along with many other provincial- and city-level labs and centers. The university enrolls 32,000 students: 13,800 undergraduates, 12,900 Master's candidates, and 5,200 doctoral candidates. Of its 2800+ faculty members, 34 are members of the Chinese Academy of Sciences and 30 are members of the Chinese Academy of Engineering. The number of students admitted to the graduate program is limited to maintain very high educational standards. Thus, each professor is limited to two new graduate students (1 PhD, 1 Master's) every year.

There are approximately 10 professors with research programs related to catalysis by nanostructured materials in various departments, such Chemistry, Chemical Engineering, Environmental Engineering, and Materials Science and Engineering. Each professor has 100 to 200 m^2 of lab space. Most of the catalysis research at the university addresses design and control of synthetic nanostructures and new applications of catalysis. Prof. Xu indicated that the Department of Chemistry of Tsinghua University is actively trying to recruit a faculty member in the area of computation and modeling.

RESEARCH AND DEVELOPMENT

Prof. Boqing Xu, Director of the Institute of Physical Chemistry of the Chemistry Department, hosted the WTEC team's visit to Tsinghua University. The 3-hour visit consisted of presentations, discussions, and a short visit to Prof. Xu's Laboratories.

Nanostructured Materials in Catalysis: Current Status and Thinking Beyond (Prof. Bo-Qing Xu)

Prof. Xu presented a comprehensive review of the research his group currently pursues. The central theme of his work is reducing the size of metal as well as support particles to improve catalytic activity and selectivity for various applications in the areas of natural gas conversion, biomass-based energy and chemicals, selective oxidation and hydrogenation, and high-performance electrocatalysis. His group is using different approaches including electrochemical methods to reduce the particle sizes of metals and their oxide support materials to optimize the properties of metal catalysts for chemical processes such as methane reforming, selective CO and alcohol oxidation, selective hydrogenation of butadiene and nitroaromatics, electrocatalysts for fuel cells, etc. His group is particularly interested in evaluating the properties of nanosized supports. They have found that the size of the support particles plays an important role in improving catalytic properties of supported metal particles, especially for Au and Ni catalysts. Attempting to emphasize the nanosize effects of the support materials, they define catalysts composed of comparably sized metal and oxide nanoparticles as nanocomposite metal/oxide catalysts.

Nanoscale Catalysis for Carbon Nanotube Synthesis (Prof. Weizhong Qian, Chemical Engineering)

Prof. Qian's research is centered on selective synthesis of carbon nanotubes (CNTs), especially single-walled carbon nanotubes (SWCNT), and understanding the CVD process to control high-temperature catalysis and coke formation. His group is involved in designing nanoscale and porous catalysts by phase separation and adding Na_2CO_3, respectively. Catalyst synthesis is designed to control the morphology of the CNTs formed. For example, they have successfully synthesized controlled-diameter tubes, CNTs filled with metal (coaxial carbon metal nanowires), SWCNTs using porous catalysts, and coiled CNTs using bimetallic catalysts (Figure C.32). Coiled tubes result from a difference in growth rates on each adjacent metal component of the bimetallic catalyst.

Prof. Yongfa Zhu (Department of Chemistry)

Prof. Zhu's research interests are divided in two categories: (1) Photocatalysts for pollution control and (2) oxidation catalysts to improve CO conversion. The research group is synthesizing mesoporous TiO_2 films with anatase structure that are highly efficient for charge separation. Mesoporous films with high surface area (10 nm pore size) result in increased activity (6 times that of smooth films) for photocatalytic degradation of formaldehyde. They have also synthesized sheets of nanostructured perovskites such as Bi_2WO_6 and Bi_2MoO_6 (Figure C.33) for photocatalysis. Nanostructured oxides are also being investigated as oxidation catalysts. For example, they found that the catalytic oxidation of CO can be improved by using a nanostructured MnO_2 catalyst.

Prof. Xun Wang

Prof. Wang's group is involved in synthesizing nanoparticle metal catalysts with controlled shape (round or cubic) and size. They are studying the reactivity of various crystal planes and are designing the crystal nanoparticles to expose particular active surface planes using surfactant templates that can be removed.

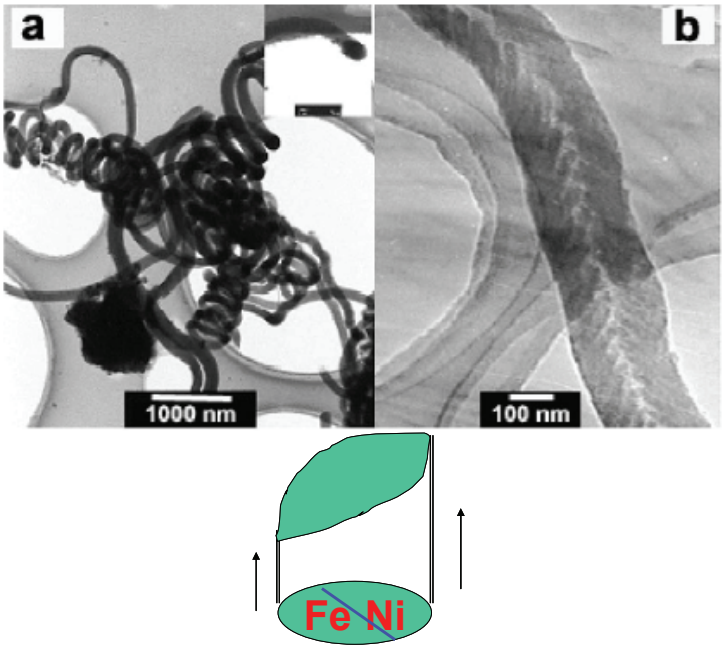

Figure C.32. Formation of coiled CNTs due to difference in growth rates on bimetallic catalyst particles (courtesy of Dr. Boqing Xu).

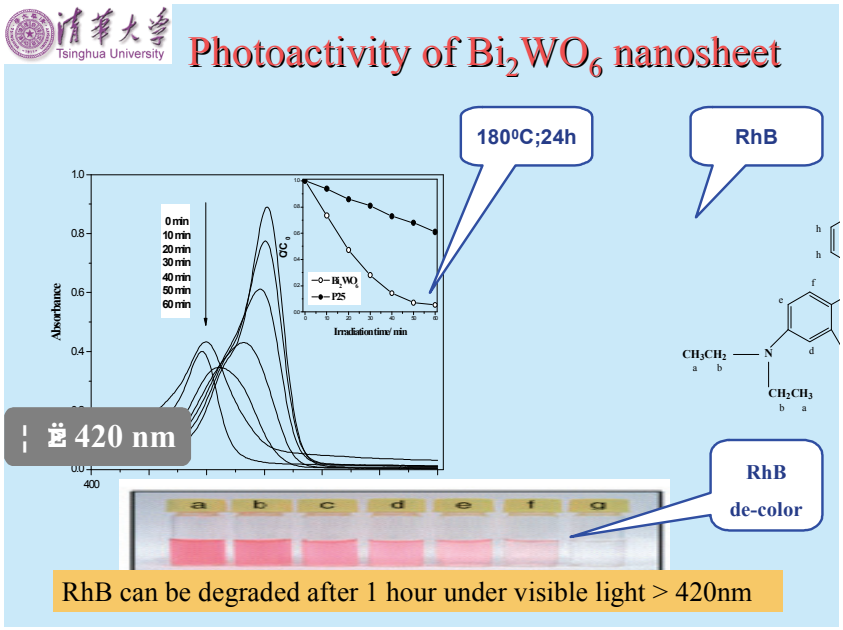

Figure C.33. Improved photoactivity of Bi_2WO_6 nanosheet (courtesy of Dr. Boqing Xu).

Prof. Duan Weng

Prof. Weng of the Department of Materials Science and Engineering is interested in automotive exhaust abatement. In particular, the issues of oxygen storage and the important role of rare earth dopants on auto exhaust catalysts are being addressed in his laboratory. This research has been performed in cooperation with Engelhard.

SUMMARY/CONCLUSIONS

The primary focus of the catalysis research at Tsinghua University is on synthesis of nanostructured metals and supports, and their applications in catalysis. Common preparation techniques such as hydrothermal synthesis, electrochemical deposition, and chemical vapor deposition are used to obtain high dispersions and nanostructured catalyst and support composites. The applications ranged from controlled synthesis of CNT, reaction of aromatic compounds, and conversion of syngas, to pollution control. Catalytic reduction of pollutants such as SO_2, NO_x, and Hg is also being investigated. There is limited effort directed towards green chemistry and renewable energy sources. There is some collaboration at the national and international level between individual research groups. They indicated strong interest for international collaboration on advanced characterization of nanostructured catalysts.

The majority of the research funding is from national sources such as the Natural Science Foundation of China, the Ministry of Science and Technology, and the Ministry of Education. A limited level (20–30%) of research is also funded by industry. The success rate for individual grants (300,000 RMB/3 years) from National Natural Science Foundation of China is quite high compared to a collaborative consortium of 40–60 researchers funded by the Ministry of Science and Technology of China at a level of 20–30 million RMB for five years.

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BACKGROUND

The University of Tokyo is one of the leading research universities in Japan and Asia. The 2005 "ARWU" rankings, drawn up by Shanghai Jiao Tong University, placed the University of Tokyo first in the Asia Pacific region. The University has 10 faculties, with a total of ca. 2,400 full-time faculty members, and 30,000 students (some 2,100 of them international) on 5 campuses in the greater Tokyo region. The university was founded in 1877 under its current name by amalgamating older government schools for medicine and Western learning. With the start of the new university system in 1949, the University of Tokyo absorbed the former First Higher School (today's Komaba campus) and the former Tokyo Higher School, which henceforth assumed the duty of teaching first and second-year undergraduates, while the faculties on Hongo main campus took care of third and fourth-year students.

The University of Tokyo has since 2004 been incorporated as a "national university corporation" under a new law that applies to all national universities. Nearly all academic disciplines are taught at the university. The university is proud of its broad alumni presence in very high-ranking positions in government, law, business, and academia, reflected in the fact that five prime ministers of Japan in recent decades have been University of Tokyo graduates.

The research in catalysis by nanostructured materials is conducted predominantly in the Departments of Chemistry and Chemical Systems Engineering. Of the 55 faculty members in these departments, ~12 are involved in catalysis. The total number of graduate students in catalysis research is about 80, with PhD students accounting for 30–50% of the total.

Funding for science including catalysis is obtained mostly from government sources. The Ministry of Education, Culture, Sports, Science and Technology is one of the major sources of funding for promoting scientific research activities in Japan in universities and other institutions. For example, in FY2003, the University of Tokyo received from this Ministry alone ¥23,880 million (or ca. $195 million) in scientific research grants. Funding from private sources, e.g., Japanese chemical industry, provides ~20–30% of the

external research support. A typical annual level of research funding per full professor stands at ca. ¥75-100 million (or ca. $600,000–$800,000), which does not include institutional overhead charges, summer faculty salary, or student stipends and tuition. The government of Japan provides student stipend and tuition support separately from these grants in a form of individual awards to graduate students.

The Departments of Chemistry and Chemical Systems Engineering participate in the "The 21st Century COE (Centers of Excellence) Program" started at the University of Tokyo in 2002. The Ministry of Education, Culture, Sports, Science and Technology established a fund to give prioritized support for the formation of global research and education centers based on the "Policy for the Structural Reform of Universities." The aims of this program are to form world-class research and education centers at universities in Japan, to cultivate creative human resources capable of improving research standards of leading the world, and to promote the building of universities of global appeal. This program covers almost all academic fields, such as mathematics, physics, life science, material science, engineering, sociology, and interdisciplinary science. Twenty-eight out of the 274 centers throughout Japan, or approximately 10% of the total, have been established at the University of Tokyo. Research and education activities are carried out at each center under the leadership of a professor and with the participation of 10 to 25 faculty members together with many graduate students. The University of Tokyo now has 4000 faculty members, and approximately one-fifth to one-fourth of those professors and associate professors participate directly in the activities of "The 21st Century COE Program."

RESEARCH AND DEVELOPMENT

During its visit to the University of Tokyo, the WTEC team met with three members of the Departments listed above and toured some of the labs. Brief descriptions of the research activities are given below.

Professor Iwasawa's laboratory (http://utsc2.chem.s.u-tokyo.ac.jp/~yiwswlab/INDEXeng.htm) focuses on three topics in his research, grouped broadly into surface science, electrocatalysis, and enzymatic catalysis. The recent focus of his research has been

- Nanoscale design of catalysts for fuel cells (e.g., Pt/C system) and automotive applications (e.g., Pt/Ce-Zr-O-based 3-way catalyst)
- Characterization of dynamic behavior of catalytic systems, e.g., Au-Ag/Si(100) and TiO_2(001)
- Real-time characterization of catalysts under *in situ* and *operando* conditions
- Development of novel X-ray synchrotron techniques in collaboration with the Photon Factory in Tsukuba and Toyota, such as time-resolved EXAFS, energy dispersive EXAFS with a 2 msec resolution, and QXAFS with a 1 sec resolution
- Current development of XAS techniques with a 10 μsec resolution

The ultimate goal of these efforts is the development of new nanostructured catalytic materials. In Professor Iwasawa's opinion, the knowledge developed in understanding the fundamentals of chemical catalytic processes will be successfully transferred over the next 10 years to other fields, such as photocatalysis, electrocatalysis, and environmental catalysis.

Research in the area of enzymatic catalysis is aimed at mimicking the structure, dynamic behavior, and function of natural biocatalysts in artificial molecularly imprinted catalytic systems. Molecular imprinting represents a new synthesis method to design new catalysts for shape-selective and asymmetric catalysis that incorporates responsive active sites by combining controllable preparation steps and DFT theory to design ligands and active sites in a surface-attached organometallic complex. Recent examples from this research include silica-supported oxo-V dimer catalysts for chiral coupling of 2-naphthol, and imprinted Rh dimer catalysts for alkene hydrogenation. The most significant challenge is reproducing enzyme-like behavior on surfaces of molecularly imprinted catalysts.

Professor Iwasawa's laboratories contain a significant amount of state-of-the-art equipment solely dedicated to catalysis research, e.g., solid-state NMR; 5 noncontact AFM, SEM, and STM units; photon emission

microscope; 3 FTIRs; 1 confocal Raman system; XRF, XRD; 1 MALDI mass-spectrometer; 32 PCs; XPS, Auger, and UPS spectrometers.

Professor Domen (http://www.chemsys.t.u-tokyo.ac.jp/laboratory_domen-kubota_e.html) is interested in catalysis for emerging energy applications, namely electrocatalysis for fuel cell applications and photocatalytic water splitting. **Professor Okubo**'s research (http://www.zeolite.t.u-tokyo.ac.jp/index_e.html) is focused on applications of zeolites in environmental catalysis. It is their shared opinion that the funding for catalysis research for individual investigators and the number of academic catalysis laboratories in Japan has remained relatively stable. According to them, the quality of international graduate students coming to Japan noticeably improved after 9/11. Another recent significant change in Japan has been that the industry realized that catalysis research was again important. Their laboratories have been successful in attracting significant governmental funding with industrial collaboration (Mitsubishi Chemical, Nippon Shokubai) for catalysis research at a level of $1.6 million per year for 5 years.

Professors Domen and Okubo indicated that energy and environmental applications will likely pave the future for heterogeneous catalysis. The most notable examples include methane conversion and coal gasification, and to a lesser degree, CO_2 utilization. Whereas large collaborative projects in the area of catalysis for energy and environment are currently encouraged by the government, so far large collaborative projects funded have been in the area of homogeneous catalysis. A current example of a larger collaborative project sponsored by the Japan Science and Technology Agency (JST) in the area of heterogeneous catalysis is a 5-year CREST (Core Research for Evolutional Science and Technology) grant awarded in 2002 to a group of 8 teams ($500K-800K/team/year) headed by Professor Makoto Misono, President of National Institute of Technology and Evaluation, on "Creation of Nano-Structured Catalysts and Materials for Environmental Conservation."

SUMMARY AND CONCLUSIONS

The University of Tokyo is a world-class research university with significant activities in both fundamental and applied catalysis research. The research groups in both Chemistry and Chemical Systems Engineering pursue a number of highly innovative research directions aimed at understanding the fundamental steps underlying the catalytic phenomena and translating this knowledge to synthesis of novel nanostructured catalytic materials. The group in Chemistry successfully blends experimental research with DFT theory of catalysis. The physical infrastructure and characterization facilities are outstanding, and the financial support for catalysis research is highly impressive.

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BACKGROUND

At University of Tsukuba the WTEC panel visited two research groups: Nakamura and Kunimori-Tomishige. This was our first visit to a Japanese university and we learned some general information about the academic situation in Japan. The average time to complete PhD and MS degrees at University of Tsukuba is three and two years, respectively, which is typical of Japan. Most BS students in Japan choose to get a MS degree also, as it is difficult to get a job without an MS degree. However, Japanese companies treat MS and PhD degrees the same in terms of pay and jobs, and therefore most students do not go on to get PhDs. Salaries for graduate students are paid by the Ministry of Education and not charged to a PI's grant. The overhead rate at Tsubuka is around 10%. Intellectual property on contracts between academia and university is usually negotiated before the contract begins. Typically, the IP belongs to the university, but industry can negotiate IP rights to IP material generated during the study. Members of both research groups indicated they felt the important themes in catalysis in the next 10–20 years will be related to energy and environment.

Background of Nakamura Research Group

The focus of Professor Nakamura's group is on surface science and catalysis. The Nakamura research group consists of 11 people, including 1 assistant professor, 2 PhD students, 6 MS students, and 2 undergraduates. The demographics of the group are 1 Korean, 1 Chinese, and the rest Japanese. The equipment includes STM, XPS, STS, and molecular beam apparatus. Japan's Ministry of Education provides funding to pay for graduate student tuition and a small living stipend. Professor Nakamura tries to supplement the stipend of his graduate students by paying them as research assistants. Professor Nakamura has strong industrial ties to automobile and chemical companies. He works with these companies to help solve industrial problems related to catalysis. He estimates that approximately 50% of his funding comes from industry and 50% from academia. His group is a balance between fundamental and applied problems; however, most of his students prefer to focus on applied problems. Professor Nakamura views the grand challenges in catalysis to be all energy-related, specifically in the areas of electrochemistry (fuel cells), biofuels, and environmental catalysis (green chemistry).

Background of Kunimori-Tomishige Research Group

The Kunimori-Tomishige laboratory focuses on green chemistry and environmental catalysis. There are three current themes in this research group: (1) design and control of synthetic nanostructured materials, (2) nanoscale characterization of catalysts in their working state, and (3) new applications of catalysis.

Currently all the members of this group are Japanese. The group contains 1 full professor (Kimio Kunimori), 1 associate professor (Keiichi Tomishige), and one technical staff member. There are 17 students in this group: 2 PhD students, 11 MS students, and 4 BS students. The group has three labs of 1180 ft^2, 650 ft^2, and 540 ft^2. The major equipment of the lab includes multiple GCs, 2 HPLC, GC-MS, UV-Vis, 4 QMS, BET, TPR & TPO systems, NO_x meter, CO_x meter, two FTIRs, TGA, TPD system, Volumetric adsorption, and SEM with EDX. Its researchers also have access to TEM (at Kanagawa University) and use synchrotron radiation techniques (at KEK-PF and SPring-8). In 2006 and 2007 they received $400,000 (¥49,000,000) in industrial support (supported by Nippon Shokubai, Chiyoda Corporation & JOGMEC, Nippon Steel Corporation, and J-Power). During this same time period they also received $480,000 (¥58,000,000) in government support from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan Society for the Promotion of Sciences (JSPS) ($150,000 from MEXT and JSPS), and the New Energy and Industrial Technology Development Organization (NEDO) ($330,000). They have two major collaborators: Dr. K. Okumura at Tottori University with whom they collaborate for *in situ* QXAFS at SPring-8, and Dr. T. Miyao at Kanagawa University with whom they work for TEM observations.

RESEARCH AND DEVELOPMENT ACTIVITIES

Nakamura Research Activities

The research projects in the Nakamura research group are associated with fuel cells and energy-related catalysis. The group has recently reported that Pt supported on carbon nanotubes is higher in activity than Pt supported on carbon black, and that it reduces the Pt usage by 60% in PEM fuel cells (Matsumoto et al. 2004). Dr. Nakamura thinks that the carbon nanotube is changing the d-band center of the Pt. His group is studying methanol synthesis and trying to identify the nature of the active site, which they claim is CuZn (Wang et al. 2006). Dr. Nakamura's group is also involved in studying the growth of carbon nanotubes (Okita et al. 2007). They also do DFT calculations (Wang et al. 2005).

Kunimori-Tomishige Research Activities

Natural Gas Conversion with Ni-Pt Bimetallic Catalysts

The Kunimori-Tomishige group is studying steam reforming of methane. They have developed a way to measure temperature gradients within the steam reforming reactor, as shown in Figure C.34. They have shown that a bimetallic Ni-Pt catalyst can decrease hot spots formed in the methane reforming reactor (Li et al. 2007). They have characterized this catalyst by EXAFS (see Figure C.35) and other techniques, including FTIR, TEM, and TPR.

Hydrogenolysis of Glycerol

This group has studied the hydrogenolysis of glycerol to 1,2 propanediol and 1,3 propanediol. They show that this reaction occurs at lower temperatures with Ru/C + Amberlyst (Miyazawa et al. 2006). They have also studied the reaction pathway (see Figure C.36) and identified acetol as a key intermediate. Their studies have identified Rh/SiO_2 as potential catalysts for 1, 3 propanediol production (Tomishige et. al. 2007). They are now starting to develop hydrogenolysis reactions for other biomass-derived oxygenated molecules.

Catalytic Tar Conversion from Biomass Generation

The Kunimori-Tomishige group is also studying the production of syngas from biomass and how to reduce the tar formation in this process. Its researchers have shown (Asadullah et al. 2002) that $Rh/CeO_2/SiO_2$ is particularly effective at converting biomass-derived tars into syngas (see Figure 8.5). They have performed QXAFS of the $Rh/CeO_2/SiO_2$ catalysts under both reductive and oxidative conditions (Figure C.37).

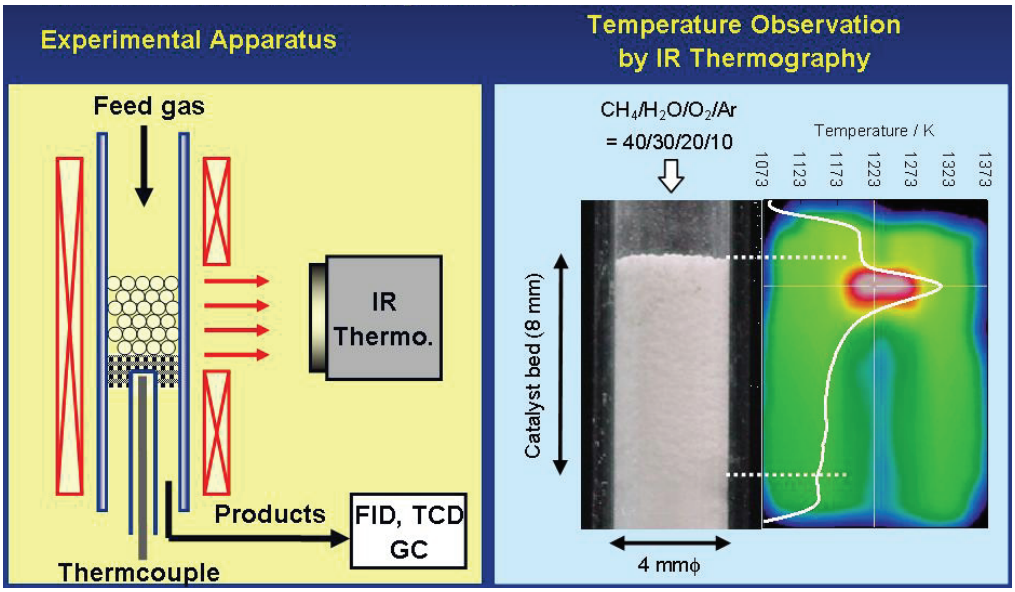
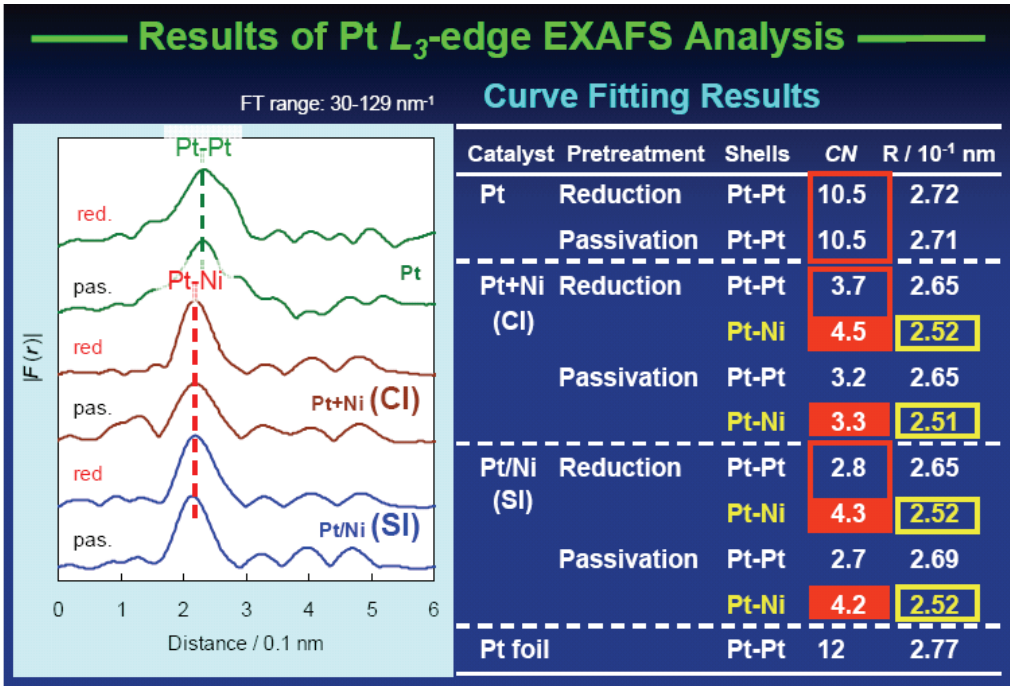


Figure C.34. Apparatus to measure temperature gradients by IR thermography for steam reforming of methane (left), and experimental results for temperature gradients for methane reforming (right) (courtesy of Dr. Keiichi Tomishige).



Catalyst	Pretreatment	Shells	CN	R / 10^{-1} nm
Pt	Reduction	Pt-Pt	10.5	2.72
	Passivation	Pt-Pt	10.5	2.71
Pt+Ni (Cl)	Reduction	Pt-Pt	3.7	2.65
		Pt-Ni	4.5	2.52
	Passivation	Pt-Pt	3.2	2.65
		Pt-Ni	3.3	2.51
Pt/Ni (Sl)	Reduction	Pt-Pt	2.8	2.65
		Pt-Ni	4.3	2.52
	Passivation	Pt-Pt	2.7	2.69
		Pt-Ni	4.2	2.52
Pt foil		Pt-Pt	12	2.77

Figure C.35. EXAFS measurements for Pt and PtNi catalysts used for steam reforming of methane (courtesy of Dr. Keiichi Tomishige).

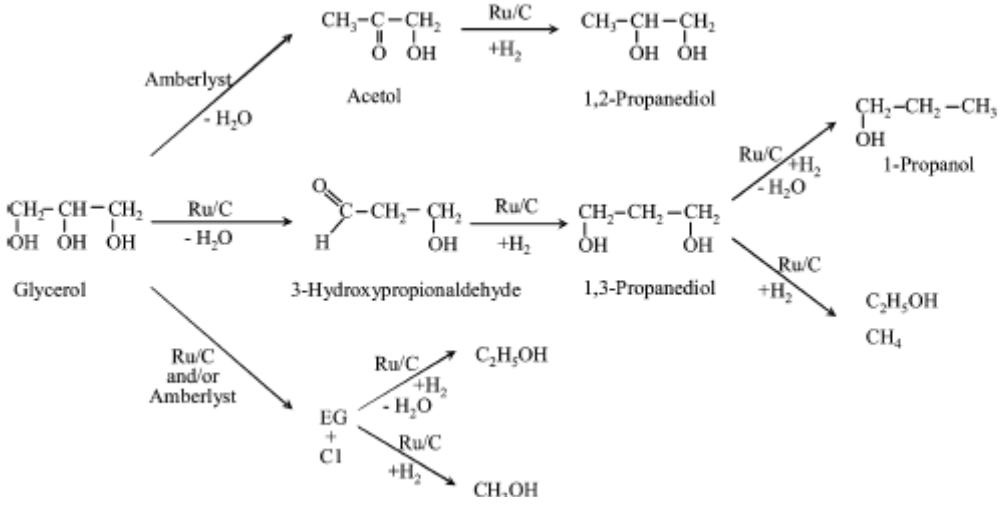


Figure C.36. Reaction scheme for conversion of glycerol over Ru/C and amerberlyst-based catalysts (courtesy of Dr. Keiichi Tomishige).

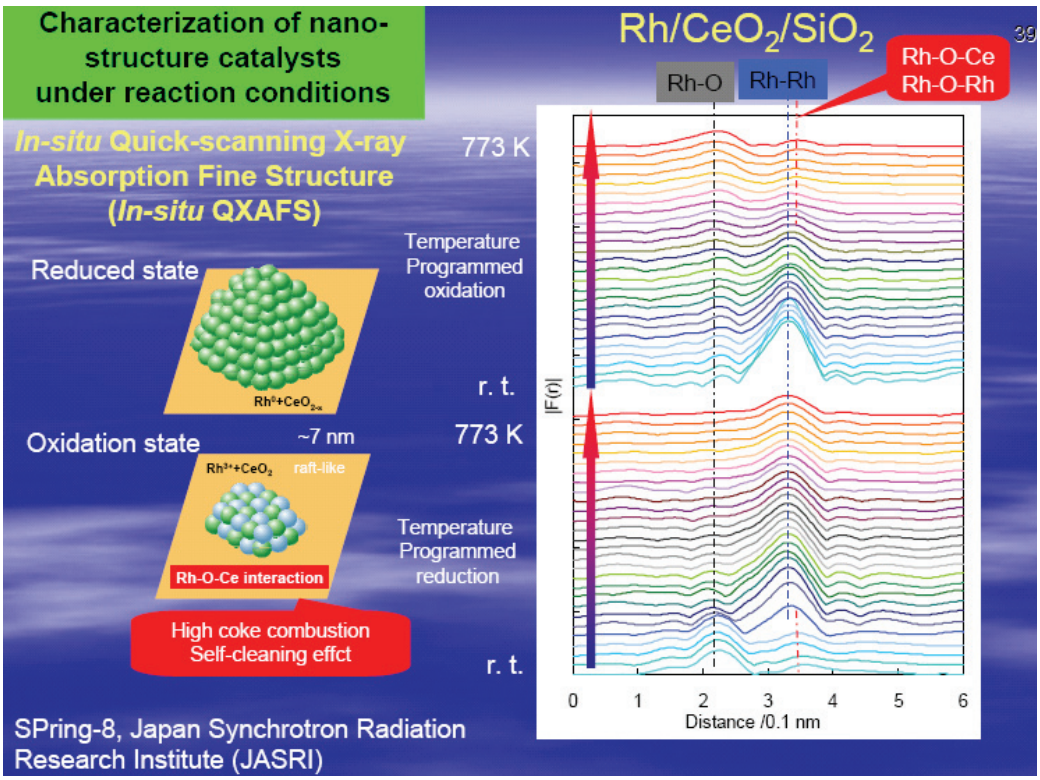


Figure C.37. QXAFS results for $Rh/CeO_2/SiO_2$ catalysts used for biomass gasification (courtesy of Dr. Keiichi Tomishige).

Mechanism of NO_x Reduction

Kunimori-Tomishige researchers are studying the selective catalytic reduction of N_2O over Fe ion dimers in zeolites (Nobukawa et al. 2004) and mechanism of NO + CO reaction. They have performed *in situ* FTIR spectroscopy to identify the surface chemistry that occurs with this reaction.

Catalytic Routes for CO_2 Utilization

The Kunimori-Tomishige group is studying methods for organic carbonate synthesis from CO_2 and alcohols catalyzed by acid-base bifunctional oxides (see Figure 6.19) (Yoshida et al. 2006).

This group views the future needs, opportunities, and direction of catalysis to be in the following five areas:

1. Renewable energy and chemicals
2. More efficient utilization of fossil fuels
3. Chemical conversion of CO_2
4. Application of new nanomaterials
5. *In situ* spectroscopic observation for the catalytic reaction in the liquid phase

SUMMARY AND CONCLUSIONS

There are a wide variety of high-quality catalysis-related activities at University of Tsukuba. The research groups are focusing on both fundamental and applied catalysis research. Researchers are using *in situ* techniques that allow the characterization of catalysts under operating conditions. They have access to state-of-the-art facilities for studying heterogeneous catalysis. These groups view energy and environment to be the key areas for catalysis in the future.

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APPENDIX D. SITE REPORTS—EUROPE

Site: **Cardiff University**
Cardiff, Wales, UK, CF10 3XQ
http://www.cf.ac.uk/

Date Visited: September 28, 2007

WTEC Attendees: G. W. Huber (report author), R. J. Davis, V. V. Guliants, R. Sharma

Hosts & Research Interests:

Professor Gary Attard (Electrochemistry, surface science, catalysis)
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Professor Michael Bowker (Catalysis, surface science, nanoscience)
Email: Bowkerm@cardiff.ac.uk

Dr. Albert Carley (Surface analysis, catalysis, surface science)
Email: Carley@Cardiff.ac.uk

Dr. Philip Davies (Surface science, nano-imaging)
Email: DaviesPR@Cardiff.ac.uk

Professor Graham Hutchings (Catalysis)
Email: Hutch@Cardiff.ac.uk

Dr. Stuart Taylor (Catalysis)
Email: TaylorSH@Cardiff.ac.uk

Dr. David Willock (Theory/modeling)
Email: WillockDJ@Cardiff.ac.uk

BACKGROUND

The total number of people at Cardiff University studying catalysis and surface science include 65 researchers, among them, 7 academics (the hosts for the WTEC team's visit); 13-post-doctoral researchers, and 45 research students. This is one of six groups in the UK that studies catalysis and surface science. In 2004/2005 these researchers published 77 papers. The current grant-holding for these researchers is £5.5 million/yr ($11.2 million/yr). Approximately 60% of the grants come from government and 40% from industry. The university negotiates with industry prior to doing research, and all intellectual property issues are open for negotiation. Some current major instrumentation for these research groups include: XPS, AFM, STM/AFM/XPS/LEED/EPR, SEM, and *in situ* XRD.

A past weakness for all groups in the UK system has been the lack of technical support for research; the Heterogeneous Catalysis and Surface Science group at Cardiff is currently addressing this problem in various innovative ways. It is also getting more graduate students from abroad; currently 30 % of its PhD students are foreign. The time required for a PhD is 3 years.

There are three major themes to these research groups:

1. Heterogeneous Catalysis
2. Nanoscience
3. Surface Science

RESEARCH AND DEVELOPMENT ACTIVITIES

During our visit the WTEC panelists heard presentations from our hosts that described the research that they are doing. Some of the research projects are described below.

Michael Bowker (http://www.cf.ac.uk/chemy/contactsandpeople/academicstaff/bowker.html)

The Michael Bowker group is at the interface between surface science and catalysis with an emphasis on surface science (see Bowker 2007 for a recent review that covers most of the group's recent surface science work). Figure D.1 shows an image from the Bowker Research Group of a Pd/TiO_2 model catalyst before and after exposure to oxygen. This figure illustrates the structural changes that can occur with a catalyst.

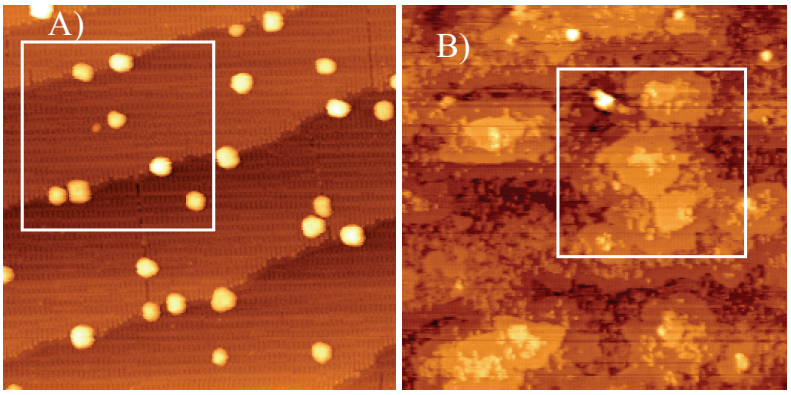

Figure D.1. Image of Pd/TiO_2 (110) model catalyst before and after exposure to 900 L of O_2 at 673 K (courtesy of Bowker Research Group).

There are four major themes in the Bowker group:

1. Oxide Surfaces and Selective Oxidation
2. Au surfaces and Catalysis/Photocatalysis
3. Automotive Catalysis and Surfaces
4. Nanoparticle Surface Science

The Bowker group claims that as nanoscience becomes more important, surface science will also become more important. Future areas of research in the Bowker group include

1. Controlled fabrication (Can we make controlled clean nanostructures by vacuum methods? Thermal stability is crucial.)
2. Identification of oxygen storage mechanism on Pt/CeO_x at the atomic scale
3. The role of peroxide in NO_x storage
4. Fabrication of Pt nanoparticles onto thin-layer BaO to investigate NO_x storage
5. Model catalysts by wet preparation techniques
6. Bio-surface interactions

Gary Attard (http://www.cf.ac.uk/chemy/contactsandpeople/academicstaff/attard.html)

The focus of the Gary Attard research group is on electrocatalysis at metal surfaces. This includes fuel cell research studying hydrogen evolution, hydrogen oxidation, oxygen reduction, and CO tolerance. Figure D.2 shows cyclic voltammetry of Ru/Pt layers from the Attard Research Group.

In situ electrochemistry experiments are also being done to study well-defined nanoparticle catalysts under "real conditions." This includes combining Raman spectroscopy with voltammetry and *in situ* STM with GC-MS monitoring of products. Another area of research for the Attard group is bio-nanoscience, which is the controlled formation of nanomaterials using bacteria.

Albert Carley (http://www.cf.ac.uk/chemy/contactsandpeople/academicstaff/carley.html)

The Albert Carley research group is using TAP with isotopic labeling to study CO oxidation with Au catalysts, supplemented by fundamental studies on model planar catalysts prepared *in situ*. Researchers in this group are using XPS to study catalysts for H_2O_2 synthesis, including TiO_2-supported Au, Au/Pd, and Pd catalysts. They have found that the most active catalyst for H_2O_2 synthesis is an Au-Pd/TiO_2 catalyst. This research indicates the importance of bimetallic catalysts. Important variables that go into designing catalysts for H_2O_2 synthesis include support, Au-Pd composition, calcination conditions, stability-leaching, and aging.

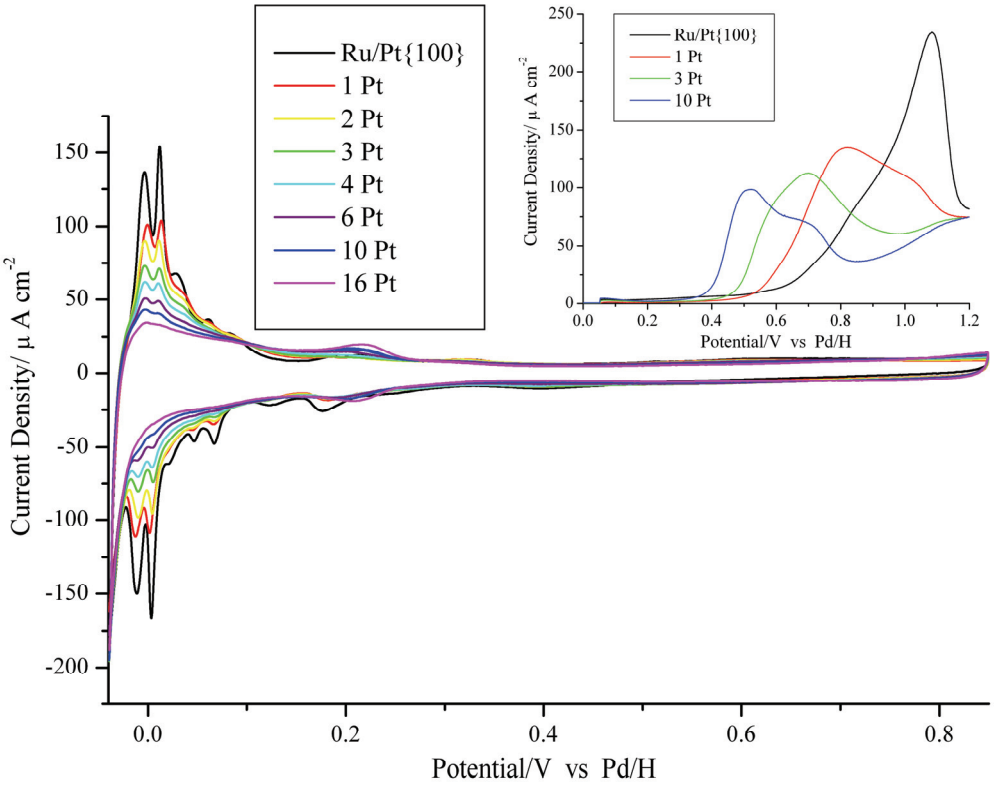

Figure D.2. Cyclic voltammetry of Ru/Pt{100} film (black line) and the platinum adlayers at 20 mV s-1. Inset displays CO oxidation peaks for selected Pt adlayers at 50 mV s-1 (courtesy of Gary Attard).

Philip R. Davies (http://www.cf.ac.uk/chemy/contactsandpeople/academicstaff/davies.html)

The Philip Davies research group uses a number of surface science techniques on model catalysts, including STM, DFT, XPS, and LEED. During the WTEC visit Dr. Davies discussed his work on understanding amine basicity on the role of reaction pathways over Cu catalysts; substrate/adsorbate mobility in the presence of Cl over Cu catalysts; and the reactivity relationships on Fe and Au catalysts. Figure D.3 shows how various surface science and theoretical techniques can be combined to give insight into the reaction surface chemistry for amine conversion over a Cu model catalyst.

Graham J. Hutchings (http://www.cf.ac.uk/chemy/contactsandpeople/academicstaff/hutchings.html)

There are three major themes for the Graham Hutchings research group:

1. Catalysis by gold
2. Oxidation with oxide catalysts
3. Enantioselective catalysts

The Hutchings research group is known worldwide for its work in the area of selective oxidations. Hutchings researchers have developed tunable gold catalysts that are able to oxidize hydrocarbons under mild conditions and also oxidize glycerol to glycerate (Carretin et al. 2002). They have also developed Pd-Au catalysts for H_2O_2 production from H_2 and O_2, as shown in Figure D.4 (Edwards et al. 2007). The highest productivity they have achieved for H_2O_2 synthesis is 900 mole H_2O_2/h-kg_{cat}. Pd-Au catalysts are also good catalysts for the selective oxidation of alcohols to aldehydes without solvents (Enach et al. 2006). The reaction for H_2O_2 synthesis takes place via –OOH species. These species are also effective for the oxidation of alcohols. This is why Au-Pd catalysts are effective for both H_2O_2 synthesis and selective alcohol oxidation.

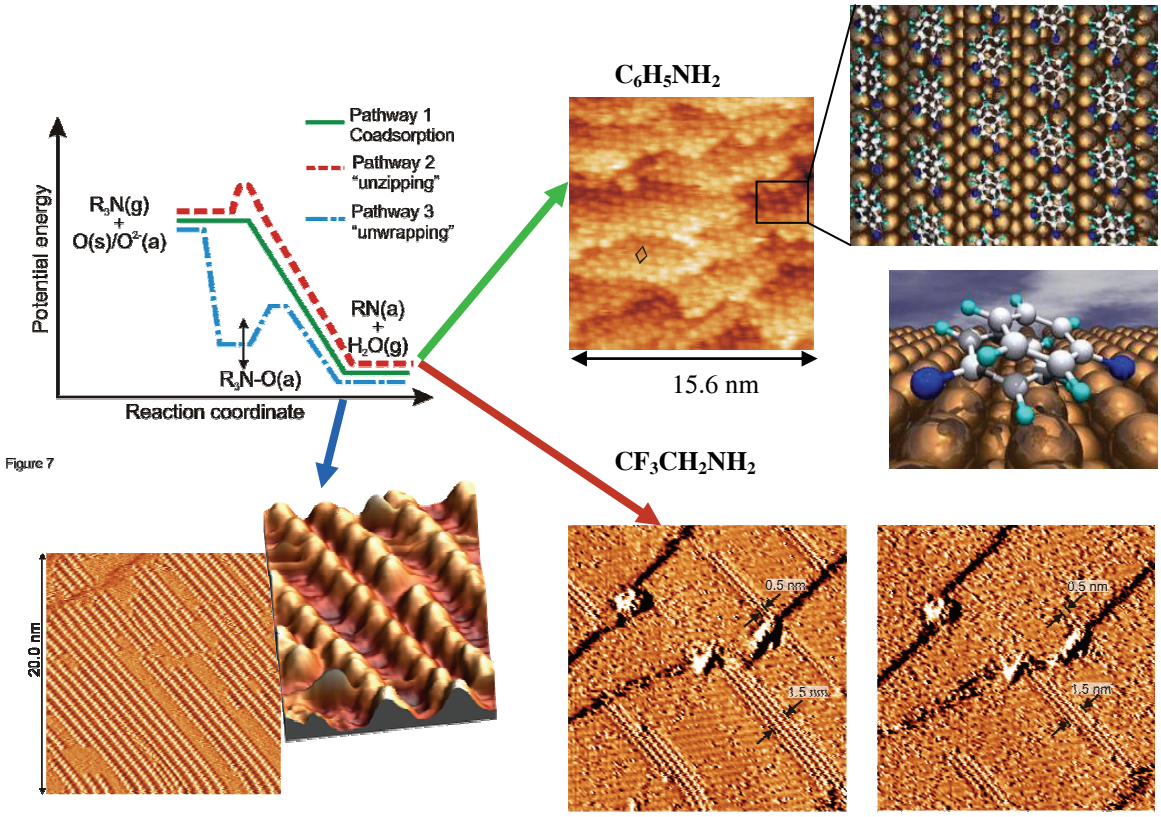

Figure D.3. Role of amine basicity in controlling reaction pathway for Cu(110): R3N(g) + O(a) → H_2O + RN(a). Results are from a combination of techniques including STM, XPS, DFT (courtesy of Philip Davies).

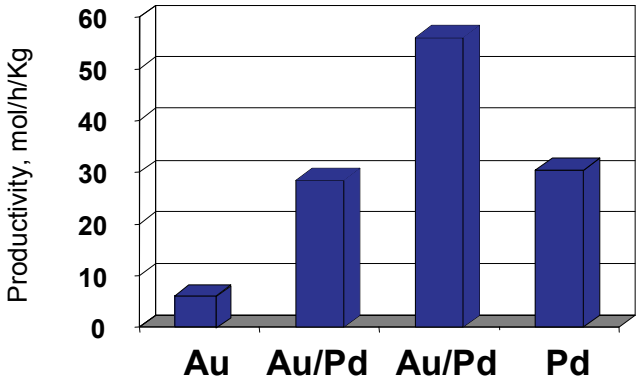

Figure D.4. Rate of H_2O_2 formation from H_2 and O_2 over TiO_2 supported Pd-Au catalysts (courtesy of Graham Hutchings).

Figure D.5 shows some of the Hutchings group work on identifying the active phase and reaction mechanism for oxidation reaction with vanadium phosphate catalysts (Conte et al. 2006).

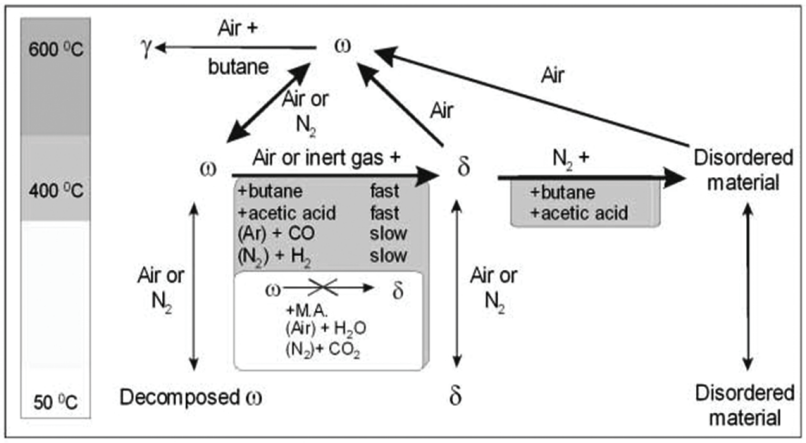

Figure D.5. Summary of w-$VOPO_4$ transformations observed between 50º and 600ºC. w-$VOPO_4$ transforms to d-$VOPO_4$ when exposed to a variety of reactants at 400ºC. A further transformation of d-$VOPO_4$ into a disordered material was observed when butane or acetic acid was added in the absence of oxygen. d-$VOPO_4$ recrystallized to w-$VOPO_4$ when calcined at 600ºC in air. The disordered material obtained in the butane experiment recrystallized to w-$VOPO_4$ when calcined at 600ºC in air. w-$VOPO_4$ transforms irreversibly to g-$VOPO_4$ when exposed to butane in air at 600ºC (Conte et al. 2006).

Stuart Taylor (http://www.cf.ac.uk/chemy/contactsandpeople/academicstaff/taylor.html)

The Stuart Taylor group is currently studying the following areas:

- Total oxidation (Ambient temperature CO and VOC oxidation)
- Selective oxidation of hydrocarbons
- Catalyst preparation (co-precipitation, supercritical preparation)
- Fischer-Tropsch Synthesis
- Hydrogenation reactions

Researchers in this group have found that nanocrystalline CeO_2 is also active for total polyaromatic hydrocarbon oxidation. They are studying selective propane oxidation with Co-oxide catalysts and have observed that nanocrystalline Co_3O_4 is extremely active for hydrocarbon oxidation. At low temperature, Co_3O_4 has a high selectivity towards propylene. These catalysts do deactivate but are easily regenerated.

David J. Willock (http://www.cf.ac.uk/chemy/contactsandpeople/academicstaff/willock.html)

The David Wilcox group uses computational chemistry to understand heterogeneous catalysis. Researchers in this group use quantum chemistry methods to understand the reaction profiles of complexes and adsorption and reaction at metal and oxide surfaces. They also use force field methods such as Monte Carlo simulations. This group has conducted studies for acetone adsorption on Pt surfaces. They have also studied methane activation on MoO catalysts (Coquet and Willock 2005). Their research indicates the important role of defect Mo sites, and without defects no activation is seen. They also teach an MS course in molecular modeling and scientific computing.

SUMMARY/CONCLUSIONS

There is a wide range of world-class catalysis activities occurring at Cardiff University, spanning surface science with model catalysis to theoretical calculations to catalysis under industrial conditions. This integrated approach allows insights into fundamental chemistry and advances in real world catalysis to be made. It is likely that Cardiff University will continue to make significant advances in catalysis in the future.

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Site: **Consiglio Nazionale delle Ricerche (CNR, Italy) and Associated Laboratories**

Date Visited: September 24, 2007

WTEC Attendees: L. Thompson (report author), J. Miller, M. Neurock, J. Regalbuto, M. DeHaemer

Host: Dr. Rinaldo Psaro, National Research Council
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BACKGROUND

During a full-day workshop at the University of Turin, the WTEC visiting team met with representatives from several Italian institutions involved in catalysis research and development. This site report covers discussions the team had with Dr. Rinaldo Psaro of the Consiglio Nazionale delle Ricerche (CNR), the National Research Council of Italy.

CNR is a public organization with the mission of promoting, disseminating, transferring, and improving research activities for the scientific, technological, economic, and social development of Italy. Interdisciplinary scientific and technological research is organized into several sectors: biotechnology, medicine, materials, environment and land, information and communications, advanced systems of production, judicial and socio-economic sciences, classical studies, and arts. The CNR facilities are distributed across the country through a network of institutes whose goal is to promote diffusion of its competencies throughout the country. Financial resources are provided primarily by the government. Nearly 30% is derived from external research grants and contracts, including contracts with the European Union and other international organizations. Catalysis research in connection with the CNR is being carried out at the following institutions:

- University of Udine (Professors A. Trovarelli, G. Dolcetti, and C. De Leitenburg; http://web.uniud.it/dstc/)
- University of Trieste: Materials, Energy, and Environment group (Professors P. Fornasiero and M. Graziani; http://www.dsch.univ.trieste.it/~fornasiero/index.htm)
- Instituto per lo Studio dei Materiali Nanostrutturati (ISMN) in Palermo (http://www.ismn.cnr.it/eng/home.htm)
- Instituto di Chimica dei Composti OrganoMetallici (ICCOM) in Florence (http://www.iccom.cnr.it/index.php)
- Instituto di Scienze e Tecnologie Molecolari (ISTM) in Milan (http://www.istm.cnr.it/)

RESEARCH AND DEVELOPMENT

Major research programs at the University of Udine focus on highly stable zirconia-supported Ag catalysts for combustion of soot (Aneggi, de Leitenburg, et al. 2006; Aneggi, Boaro, et al. 2006) and novel water gas shift (WGS) catalysts. The WGS catalysts include CeO_2- and ZrO_2-supported Au and Pt catalysts (Tibiletti et al. 2006). For the CeO_2-supported catalysts, the support surfaces are being modified to enhance the ability to oxidize CO using oxygen released from water reduction. In particular, methods are being developed to preferentially expose the more active {100} surfaces (vs. {111} surfaces), as shown in Figure 6.12 (Aneggi et al. 2005). Carbon monoxide oxidation is a key step in the redox mechanism for WGS.

Major research programs at the University of Trieste focus on the purification of reformate using preferential oxidation (PrOx) and WGS reactions, the design of photocatalysts and development of mixed oxide cathodes for solid oxide fuel cells (SOFC) (Bevilacqua et al. 2006). In an effort to enhance the stability of reforming PrOx and WGS catalysts, methods have been developed to encapsulate preformed metal nanoparticles with porous oxide layers (Montini, De Rogatis, et al. 2007; Montini, Condò, et al. 2007; Esch et al. 2005). These nanostructured materials would allow the reactants and products access to the catalytically active metal (Rh, Au, Ni, Cu, etc.) while inhibiting sintering. Titania based materials are being doped with B and N to reduce the band gap thereby increasing the quantum efficiency (Bettinelli et al. 2007). Related photocatalytic materials are being developed for the production of hydrogen from ethanol/water solutions (see Figure D.6).

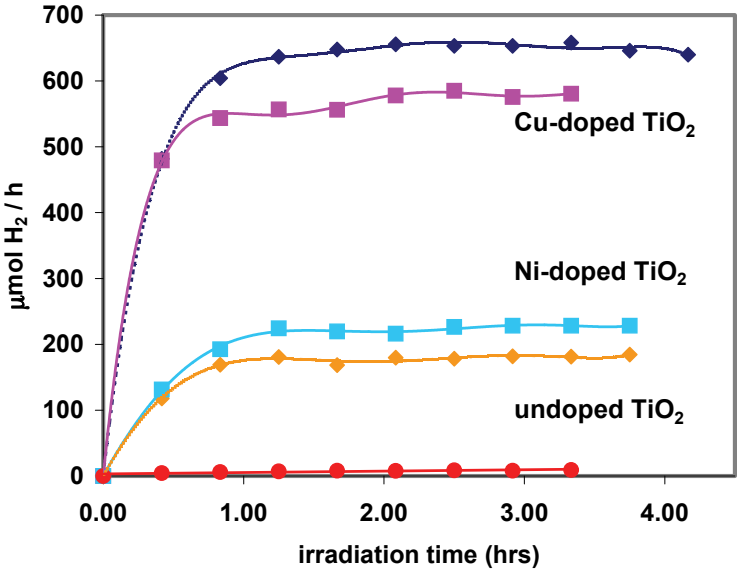

Figure D.6. Hydrogen production by metal-doped titania photocatalytic materials (unpublished data; reproduced with the permission of the authors, R. Psaro).

Major research programs at the ISMN focus on synthesis of supported catalysts, synthesis of mesoporous ordered supports, application of novel catalytic materials in fuel upgrading and pollution control, and development of structure-reactivity relationships. Bimetallic and trimetallic catalysts of Co, Au and/or Pd supported on HMS (Hexagonal mesoporous silica) have been synthesized and tested in the thiophene hydrodesulfurization (HDS) reaction (Venezia et al. 2007a). These materials were more active than analogous materials prepared using either amorphous silica or siliceus MCM-41 as supports. The superior activity, in particular for the monometallic Pd/HMS catalyst was explained on the basis of a bifunctional mechanism involving the acid sites of the support (see Figure 6.7). Sol-gel-derived oxides are being developed to improve the thermal stability of three-way exhaust and deNO_x catalysts. In addition, mixed oxides are being designed as supports for Pd and Pt catalysts used for the total oxidation of methane. This research aims to reduce the noble metal loadings and improve the catalyst tolerance towards sulfur-containing molecules (Liotta et al. 2007a and 2007b; Venezia et al. 2007b).

Major research programs at the ICCOM focus on catalysts for reforming and steam reforming reactions, electrocatalysts for direct ethanol fuel cells, water and ammonia electrolyzers and chemicals production, catalysts for hydrocarbon conversion reactions such as hydrogenation, HDS and oligomerization. Ethanol steam reforming is accomplished using an Al_2O_3 supported catalyst containing Fe, Ni and Co. This material possessed good activity at 400–500°C, producing hydrogen and a mix of hydrocarbons and oxygenates (see Figure D.7). An electrocatalytic process occurring in a direct alcohol fuel cell has been demonstrated to convert ethanol, ethylene glycol, glycerol, and other polyalcohols into carboxylic acids with concomitant release of electricity. For example, glycerol was converted to a mix of glyceric acid, tartronic acid, glycolic, oxalic acid, formic acid, CO_2, and electricity at potentials up to 0.4 V. The maximum power density was 48 mW/cm^2 at 0.25 V.

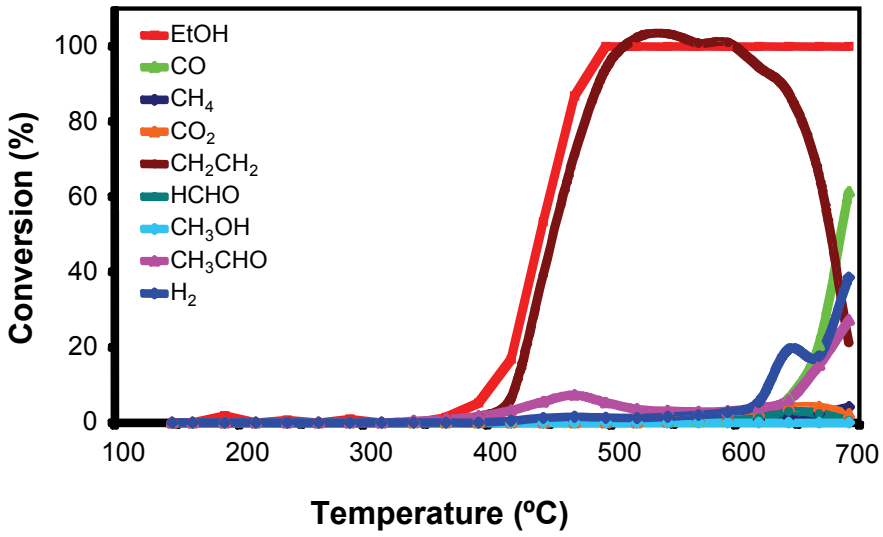

Figure D.7. Performance of Al_2O_3 supported catalyst containing Fe (0.30%), Ni (0.27%), and Co (0.28%). The gas hourly space velocity is 200,000 hr^{-1} and the ethanol:water ratio is 1:5 (courtesy of the authors, R. Psaro).

Major research programs on nanostructured catalysts at the ISTM and ICCOM focus on hybrid catalysts (Bianchini et al. 2003; Barbaro et al. 2006), the preparation of nanosized bimetallic particles deposited onto inorganic oxides (Guidotti et al. 2006), single-site nanostructured catalysts for the selective oxidation of fine chemicals and renewable natural products (Guidotti et al. 2003; Kholdeeva et al. 2007), the preparation of nanostructured Rh catalysts for hydrogen production (Beretta et al 2008, Dal Santo et al. 2008; Figure D.8) and the development of *in situ* and *operando* characterization tools, including a facility for diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy-mass spectrometry (Dal Santo et al 2005), and X-ray absorption fine structure (XAFS) spectroscopy. The hybrid catalysts combine anchored Rh complexes and palladium nanoparticles on the same support, mainly mesoporous silicas. The resulting catalysts can yield enhanced activities and selectivities. Analogously, Ir-Sn-based nanoparticles supported on mesostructured silicas were obtained by immobilizing bimetallic organometallic clusters. The catalyst was reported to have good activity and high selectivity for the dehydrogenation of propane to propene (Figure D.9).

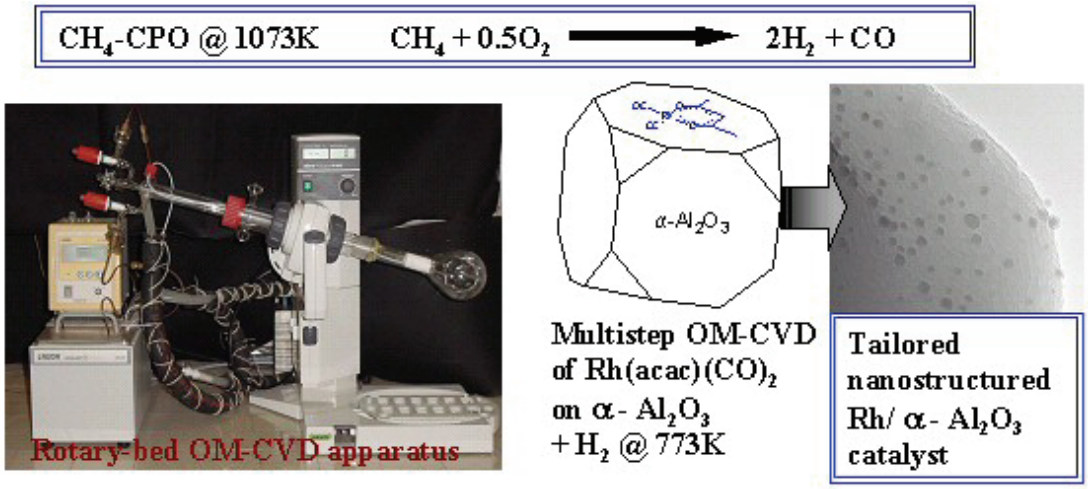

Figure D.8. Rotary-bed OM-CVD apparatus and Rh/ α-Al_2O_3 catalyst for CH_4-CPO (courtesy of CNR, R. Psaro).

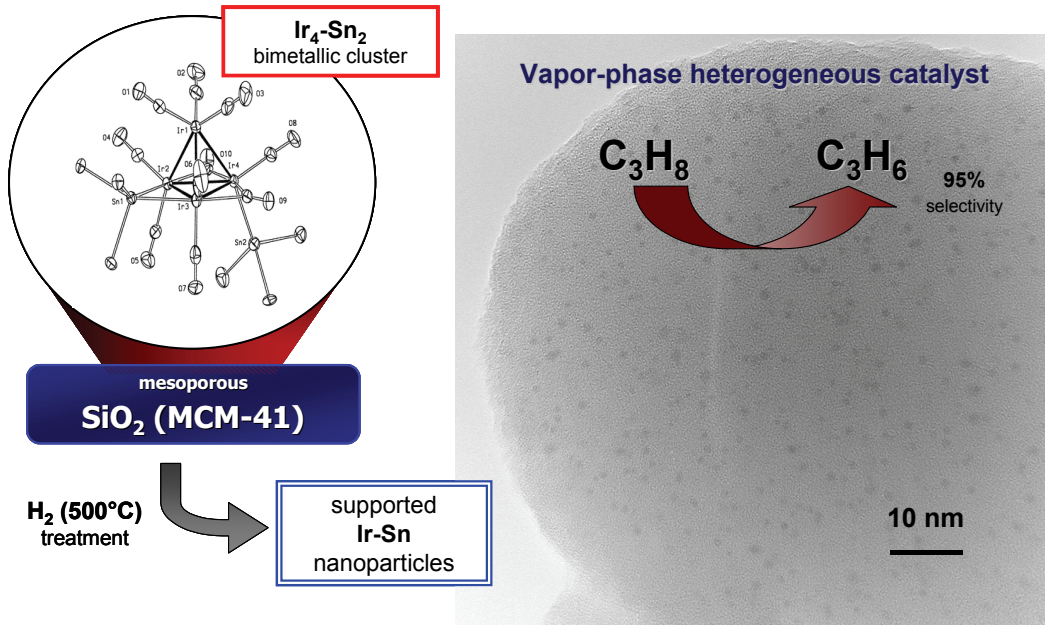

Figure D.9. Catalytic dehydrogenation of propane over cluster-derived nanostructured Ir-Sn/SiO_2 catalysts (courtesy of CNR, R. Psaro).

SUMMARY AND CONCLUSIONS

Research at the CNR and affiliated laboratories covers a number of key areas in catalysis. This work appears to be very well coordinated and well supported.

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BACKGROUND

Founded in 1829, the Technical University of Denmark (DTU) is a leading technical university in northern Europe and benchmarks with the best universities in the world. Catalysis research at DTU is concentrated mainly in three centers: The Center for Individual Nanoparticle Functionality (CINF, directed by Professor Ib Chorkendorff); The Center for Atomic-scale Materials Design (CAMD, directed by Professor Jens Nørskov), both at the Department of Physics; and the Center for Sustainable and Green Chemistry (CSG, directed by Professor Claus Christensen at the time of the WTEC team's visit) at the Department of Chemistry.

CINF, CAMD, and CSG are closely interacting groups with a large number of common research projects. CINF predominantly focuses on experimental surface science aspects, characterization, hot electron chemistry, and electrochemistry. CAMD concentrates on atomic-scale computer simulations. CSG (which was terminated in the summer of 2008) primarily specialized in the synthesis and testing of model catalysts and the development of green chemistry processes. The three centers therefore covered the key aspects necessary for the rational conception of new catalytic materials for heterogeneous catalytic and electrochemical reactions. CINF, CAMD, and CSG each have a number of industrial partners in addition to close ties to the local catalyst producer Haldor Topsøe A/S (HTAS), which is located two miles from the DTU campus. The WTEC team visited only CINF and CAMD for the present evaluation.

CINF currently has 6 senior scientists, 6 technical staff, 9 post-docs, 18 PhD students, and 3 project students. Approximately one-third of the PhD-students are funded by industry. CAMD currently has 8 senior scientists, 3 technical staff, 13 post-docs, 18 PhD students, and 10 project students. Both CINF and CAMD have an international advisory board that oversees and advises with regard to current research and future strategies. CINF was established by the Danish National Research Foundation, and CAMD was established by The Lundbeck Foundation, which is a private foundation that serves as the holding company for two of the largest medicinal companies in Denmark. These foundations still provide the largest single contributions ($1 million/year each) to the funding of CINF and CAMD, but most of their funding comes from approximately 50 smaller external research grants and company collaborations. These other sources of funding include grants from the Danish research agencies FTP and FNU; the Strategic Research Council (SRC); EU grants; Public Service Obligation; The Copenhagen Graduate School for Nanoscience and Nanotechnology (C:O:N:T); the Ministry of Science, Technology, and Innovation (VTU); Haldor Topsøe A/S: and Oticon A/S. Other industrial partners include several Japanese, British, and German companies. Generally, DTU owns the intellectual property rights on the research that the companies fund, but a trend is becoming more common that the companies wish to pay significantly more in order to keep full IP ownership.

RESEARCH AND DEVELOPMENT

Danish National Research Foundation's Center for Individual Nanoparticle Functionality (CINF)

Prof. Chorkendorff (Director, CINF) presented an overview of CINF. The general theme for the research at CINF is the fundamental study of functionality of nanoparticles initially, with particular focus on reactivity of relevance for catalysis used in connection with Environment and Energy production. The research themes of CINF involve both experimental and theoretical approaches and are focused on surface reactivity. The main purpose is to establish a close and unambiguous correlation between the morphology and the reactivity identifying the reactive site. One example is the newly understood hydrogen-induced CO splitting over transition metal surfaces (Andersson et al. 2008); in another example, they have demonstrated that monoatomic steps may be nine orders of magnitude more efficient for nitrogen dissociation than normal surface sites (Dahl et al. 1999). Some questions that are now being addressed include how many of those sites exist on given catalytic nanoparticles, How can their presence be controlled, and what is the general validity of this for catalysis?

The CINF research also includes entirely new areas, such as demonstrating new concepts where nanostructures can be created to catalyze chemical reactions under nonthermal conditions, operating on entirely different physical principles than current technology. This project involves use of ballistic electrons for enhancing surface reactivity. The experimental group focuses on controlling reactivity of surfaces ranging from well-defined single-crystal-and nanoscale clusters by utilizing standard UHV surface science methods combined with high-pressure cells to synthesize high-surface-area catalytic materials, which can be characterized and tested both in connection with heterogeneous catalysis and electrochemical reactions. The laboratory covers a wide range of experimental methods XPS, AES, LEED, TPD, IR, HREELS, PM-IRAS, SEM, STM, XRD, XRF and ISS. Special emphasis is put on development of mass selected cluster deposition in the range 1-8 nm of various metals, and construction of new microreactors on chips by MEMS technology is being explored for increased efficiency and testing of catalytic materials. CINF is developing microreactors by combining MEMS, lithography, and PVD techniques, as shown in Figure D.10. Gas inlet, outlets, and catalyst chambers are etched using MEMS technology (DCNCHIP), and a reactor can be placed in a UHV system to study reaction rates. It is also connected to a mass spectrometer to obtain the gas composition.

Another very active research area at CINF (resorting under Jane Nielsen) is the synthesis, characterization (using XPS and STM under UHV conditions), and property measurement of new catalysts for hydrogen production, such as e.g. PtBi and MoS_2 catalysts on Au (Greeley et al. 2006; Jaramillo et al. 2007).

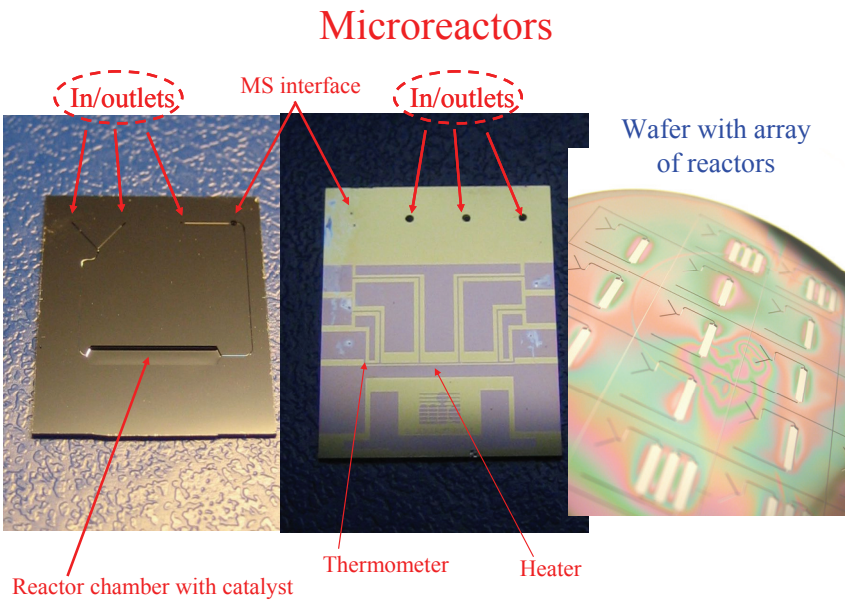

Figure D.10. DTU microreactor (courtesy of Prof. Ib Chorkendorff).

Center for Atomic-Scale Materials Design (CAMD)

CAMD, headed by Prof Nørskov (on sabbatical leave at the time of the WTEC team's visit), forms an integral part of the catalysis research at DTU. Prof. Bligaard presented the center and its research objectives. The over-all goal of the center is to develop methodology that enables the systematic computational design of new materials and functional nanostructures. The expertise of the Center includes the development of electronic structure methods to describe materials and the development of models and theory to understand them. The methods are applied to the study of surface processes including catalysis and electrochemistry, molecular electronics, energy storage materials, biomolecular structure and function, and the mechanical properties of materials. The electronic structure computer codes developed in the group are available as open source software and are used in more than 100 institutions around the world. The group has contributed to the development of the description of exchange-correlation effects in density functional theory calculations by developing functionals for use in surface physics and chemistry and by introducing methods to evaluate the accuracy of such calculations. In the area of surface chemistry and heterogeneous catalysis, the group has developed a number of concepts used in describing such processes including the so-called d-band model, the theory of structural effects in metal catalysis, the electrostatic theory of poisoning and promotion, Brønsted-Evans-Polanyi relations in surface chemistry, scaling relations between adsorption energies for different molecules (Abild-Pedersen et al. 2007), and a general theory linking energetics and kinetics (Honkala et al. 2007). The group recently developed a new set of methods allowing a theoretical description of electrochemical processes (Nørskov et al. 2004; Hinnemann et al. 2005; Karlberg et al. 2007). Currently, CAMD is using a large effort which is focused on the theory-guided design of new heterogeneous catalysts and electro-catalysts. In the related area of enzyme catalysis the group published some of the first detailed computational descriptions of the function of nitrogenases. The function of hydrogenases and photo-systemII has also been treated.

Dr. Bligaard went on to present the catalytic systems that are currently being focused on at CAMD, such as carbon chemistry processes (Substitute Natural Gas, Fischer-Tropsch, methanol synthesis, selective oxidation, and steam reforming), hydro-treatment (HDS), nanoparticular catalysis (especially Aux reactivity for x<100), zeolite reactivity, fuel cell catalysis, hydrogen evolution, Haber-Bosch synthesis (catalyst screening and alkali promotion), and ammonia decomposition. Theoretical screening is followed by experimental testing. Examples of such studies include measurement of surface and step-edge reactivity of single crystals, bimetallic and alloyed surfaces, electrochemical activity at a standard hydrogen electrode, and

theoretical determination of the shape and reactivity of nanoparticles. The group has computationally designed a new Fe-Ni methanation catalyst which performs better (and is less expensive) than the industrial Ni catalyst (Andersson et al. 2006).

The electronic transport and method development group at CAMD (presented by Dr. Thygesen) is working on understanding the functioning of single-molecule junctions for electronic applications. Systems under investigation currently are metallic nanoscale contacts (formation, chemical, structural, electronic properties), single-molecule junctions (role of coupling to electrodes, effect of side groups on the conductance), nanotubes (impurity scattering and functionalization for sensor applications), and graphene (impurity scattering, edge effects).

DTU is also an active partner (for solid state theory and computation) of the International Research and Education program for Conversion of Biomass into Fuels, Chemicals, and Materials.

SUMMARY AND CONCLUSIONS

Catalysis research at DTU is interdisciplinary in nature; the general theme of research is the fundamental study of the functionality of nanoparticles with a focus on reactivity. The overall approach is to combine experiments with theory and can be divided into two main topics: structure and reactivity, and non-thermal reactivity. Research support is provided by a wide spectrum of national, international, and industrial sources,. Similarly, collaborative efforts also include local (within DTU), European, and international partners from both academia and industry. CINF's synthesis setup includes using cluster source for depositing nanoclusters using SEM/STM apparatus where size and morphology of clusters can be visualized *in situ*. One of the strengths of DTU's integrated research programs is state-of-the-art characterization and reactivity measurement facilities combined with a state-of-the-art computational modeling platform. A new Center for Electron Nanoscopy will have *in situ* measurement capabilities using environmental SEM and TEM.

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BACKGROUND

Much of the catalysis research at the Eindhoven University of Technology (TU/e) is carried out in the Inorganic Chemistry and Catalysis Research Group. This group has active projects in the areas of Molecular Heterogeneous Catalysis, Physical Chemistry of Surfaces, Electrocatalysis, and Homogeneous Catalysis and Coordination Chemistry. Catalysis is also a theme in other research groups, such as the laboratories of Reaction Engineering and the extensive Polymer Science and Engineering groups of the Department. All groups participate in the cross-cutting organizational structure that focuses on catalysis research at TU/e, the Schuit Institute of Catalysis. The institute was named after Professor George Schuit, the first professor of catalysis in Eindhoven and the first full-time professor in catalysis in the Netherlands. He worked for Shell at Amsterdam until 1961, when he became Professor of Inorganic Chemistry and Catalysis at TU/e. After his retirement in 1977, he moved to the University of Delaware, where he was active until 1984. Schuit is well-known for his work in oxidation and hydrodesulfurization catalysis, and his interest in the theoretical basis of catalysis. His book entitled *Chemistry of Catalytic Processes* (co-authored with Bruce Gates and Jim Katzer) is a classical textbook in the field.

The Schuit Institute of Catalysis was founded in 1989 as a collaboration between several TU/e research groups interested in catalysis. Initially, its missions were to enhance visibility for catalysis, emphasize its relevance within the university, and provide a basis for attracting substantial funding from varied sources. Industrial relevance and collaboration with industry are key ingredients for success at the institute. For example, work in the area of electron and hydrogen storage is directed by someone that spends 3 days a week at Phillips and 2 days at TU/e. Another example of successful collaboration with industry is the joint research with SASOL South Africa on Fischer-Tropsch chemistry, in which SASOL regularly sends employees to TU/e to carry out research and to qualify for the PhD degree. Companies wield significant political power in the Netherlands and have been strong advocates for academic research. Approximately one start-up company is spun off from TU/e annually, including Hybrid Catalysts, B.V., a company started to commercialize hybrid catalysts. The Schuit Institute of Catalysis, which was started and initially sustained by Professor Rutger van Santen, also provided the basis for national organization of catalysis research. The Netherlands Institute for Catalysis Research (Nederlands Instituut voor Onderzoek in de Katalyse or NIOK) was establish in 1991 and links the major catalysis groups of seven Dutch universities. Professor van Santen served as its first director.

Research at the Schuit Institute of Catalysis is supported by a mix of government and industrial support, including funds from the Netherlands Institute for Catalysis Research (NIOK).

The Laboratory of Inorganic Chemistry and Catalysis at the Eindhoven University of Technology currently has 3 full time professors, 8 scientific staff, 13 post-doctoral researchers, and 35 PhD students. Its three main

groups are (1) Molecular Heterogeneous Catalysis, headed by Professor Van Santen; (2) Physical Chemistry of Surfaces, headed by Professor Niemantsverdriet; and (3) Homogeneous Catalysis and Coordination Chemistry, headed by Professor Vogt.

RESEARCH AND DEVELOPMENT

Most of the discussion centered on several major challenges confronting the catalysis community:

- Prediction of the catalytic function of materials, including those under the influence of liquids (e.g., electrocatalysts)
- Design and synthesis of better performing catalysts and catalysts for new applications
- Closing the ”meso-gap”
- Building interface between homogeneous and heterogeneous catalysis (hybrid catalysts)
- Conversion of CO_2 to useful products (mentioned by the WTEC team’s hosts as the greatest challenge)

Addressing these challenges will require better interfaces between surface science and computational/modeling efforts, improved control of nanomaterial composition and structure, advances in computational science, and rational design of new catalytic reactions and materials.

With regard to CO_2 conversion, Professors van Santen and Niemantsverdriet noted that many approaches should be explored, including the production of inorganic carbonates. One reaction to consider occurs in deep ocean vents. This reaction involves $CO_2+H_2S \rightarrow COS+H_2 \rightarrow HC$, and in nature, the heat needed to drive the reaction is provided from the high-temperature vented gases. One might use solar or other renewable sources. The efficient exploitation of solar energy requires development of new materials to enable the conversion of the entire solar spectrum into suitable energy carriers, such as electrons and hydrogen.

The central theme of the Van Santen group is to develop predictive methods and theories that relate catalyst performance to catalysis structure and composition and to design new catalytic systems to resolve key technological problems. The work is organized in four subthemes:

Theme 1: Theoretical Catalysis

The program deals mainly with the theoretical study of the mechanism of reactions taking place on transition metal surfaces, zeolites and sulfides. The main tool applied is periodical DFT, to compute transition states, ground states and vibrations, providing access to free energy values. The main tool developed in the group is the kinetic Monte Carlo method that is used to solve the many body problem of interacting reaction species on the catalyst. The overall rate of a catalytic reaction is computed based on the dynamics of reaction events of interacting particles.

Some of the reaction mechanisms elucidated are CH_4 activation, the C-C coupling reaction in the Fischer-Tropsch reaction, selective oxidation of ammonia and zeolite-catalyzed reactions. A general theory has been formulated with rules on transition state structure and transition state energy. Detailed studies have been performed on the structural dependence of the ammonia oxidation reaction. A strong collaboration has developed with the electrocatalysis program. Zeolite research focused on the elucidation of cavity effects. The concept of a pretransition state has been introduced. Moreover, a theory of reactivity of weak Lewis acids has been developed. Methods have been implemented to compute the vibrational frequencies of adsorbed molecules including anharmonic effects. In hydrodesulfurization catalysis a solid state chemical explanation of promotion in MoS_2 catalysis has been given. CP-MD studies and molecular mechanics studies have been initiated to study elementary steps in zeolite synthesis.

Theme 2: Heterogeneous Catalysis

This program is directed towards the exploration of heterogeneous catalytic systems and physical chemical studies to understand the catalytic action of working heterogeneous catalysts.

An important topic was the development of environmentally-useful selective low temperature ammonia oxidation catalyst to nitrogen. Most successful are Cu/Ag alloy catalysts dispersed in zeolites.

In zeolite catalysis, research was initiated to produce ethylene and propylene selectively from alkanes. A substantial effort has been expended to produce gallium-containing zeolites with optimum dispersion. Substantial progress was made in the understanding of chemistry and reactivity of small gallium oxo clusters in microporous zeolites. Based on in-situ spectroscopic measurements, insight from quantum-chemical calculations and kinetic data, improved reaction conditions were formulated. Another topic in zeolite catalysis was the decomposition of nitrous oxide, which is related to selective phenol production. Important results are the different site requirements for the reaction and the role of co-promotion by extraframework Al species in the reaction catalyzed by Fe^{2+}.

In addition to physico-chemical characterization and spectroscopic in-situ studies with Raman spectroscopy and solid state NMR spectroscopy, an important supporting technique developed at the TU/e is the use of Positron Emission Profiling. Applied to ammonia oxidation catalysis, it demonstrated the key role that co-adsorbed oxygen and OH plays to activate ammonia. In zeolite catalysis this technique was used to study diffusion of mixtures of branched non-branched alkanes.

Theme 3: Catalyst Synthesis

An important system that can be considered intermediate between organometallic complexes and solid state materials is that of the silsesquioxanes. Based on these materials new epoxidation catalysts have been developed. Incorporation of such catalysts into polymer matrices or pretreated microporous materials enabled researchers to exploit hydrophobic/hydrophilic interphase effects. An extensive program has been developed to apply SAXS/WAXS to analyze ordered and disordered microporous systems. Their porosity is determined by the use of a variety of amphiphilic structure directing molecules. Systems consisting of hollow spheres of varying dimensions have been made. A theory of diatom silica formation has been proposed.

Theme 4: Electrocatalysis

The electrocatalysis research is divided into two main streams:

1. Electrochemical energy storage (chair, Prof. Dr. P. H. L. Notten, part-time professor, Philips Research) is aimed at knowledge transfer in the field of both rechargeable and non-rechargeable batteries and fuel cells to support the growing societal and technical relevance of these devices in the future. Research is aimed at developing, improving and eventually implementing new and existing battery and fuel cell models, by multidisciplinary approach combining electrochemistry, mathematics and electronics. There is also an interest in improving energy storage systems.

2. Research in low-temperature fuel cells (chair, Dr. F.A. de Bruijn, part-time associate professor, Energy Research Centre of the Netherlands, ECN) primarily aims at unraveling degradation mechanisms in low-temperature fuel cells for mobile and stationary applications by a combination of electrochemical and surface-sensitive techniques. In addition, there is a project on the electrocatalysis in polymer-electrolyte-based electrolysis.

HIGHLIGHTS OF RECENT RESEARCH

Elucidation of the mechanism of nitric oxide reduction by heme and protein-modified pyrolitic graphite electrodes

Heme-modified electrodes have been shown to reduce nitric oxide to hydroxylamine with 100% selectivity, depending on pH (see Figure D.11). This is in sharp contrast to heme-based NO reductases (which make N_2O) and transition-metal electrodes, which make mainly ammonia (de Groot et al. 2005).

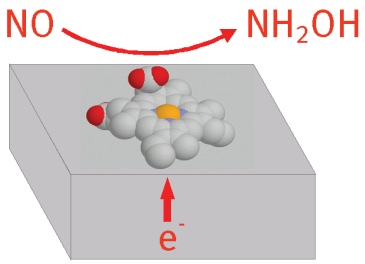


Figure D.11. Reduction of nitric oxide to hydroxylamine by heme and protein-modified pyrolitic graphite electrodes.

The role of lateral interactions in surface reactions

Researchers have shown the immense importance of lateral interactions (i.e., interactions between adsorbates) for surface reactions. They have performed various kinetic Monte Carlo simulations of realistic systems in which the behavior could only be explained with lateral interactions, e.g., Figure D.12 shows the structure of a chiral adlayer of bitartrate on Cu(110). The typical bundles of three rows of molecules could be explained by a mechanism of lateral interactions that is based on the stress in the substrate induced by the bidentate adsorption mode of the bitartrate.

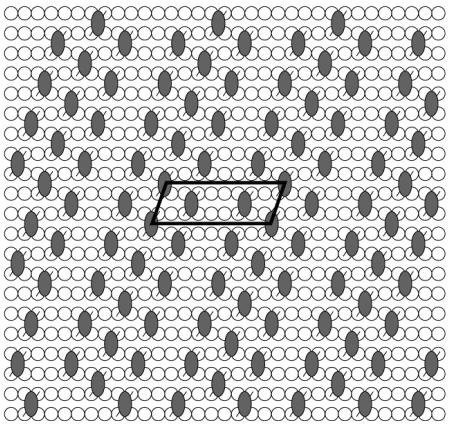
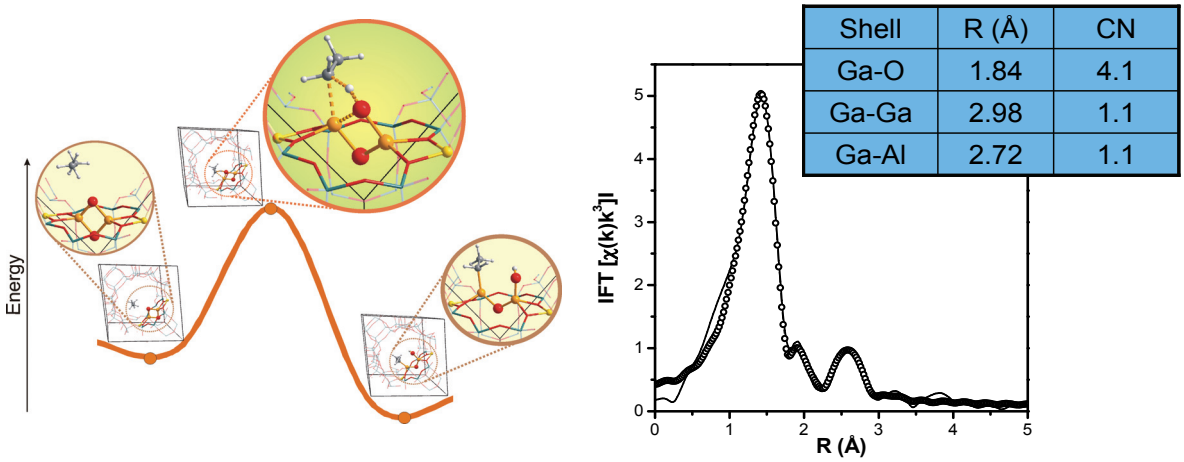


Figure D.12. Structure of a chiral adlayer of bitartrate on Cu(110).

Enormous progress has been made in the determination of values for lateral interactions.. On the one hand researchers have been able to extract lateral interactions from kinetic experiments using a combination of kinetic Monte Carlo simulations and methods from evolutionary computation. On the other hand they have developed a statistical analysis tool to determine which lateral interactions can be computed accurately with density-functional theory. The former method works better for weak interactions of the order of thermal energies. The latter works better for stronger interactions that are relevant at high coverages of the adsorbates (Hermse and Jansen 2006)

Self-repair by water during alkane dehydrogenation by gallium-containing zeolites

The mechanism of catalytic dehydrogenation of alkanes by Ga-containing zeolites has been elucidated by experimental studies, with well-defined catalysts prepared by an organometallic precursor, and quantum-chemical calculations. *In situ* X-ray absorption spectroscopy (Figure D.13, right) shows the predominant presence of Ga_2O_2 cations coordinating to the zeolite framework as highly active dehydrogenation species. Such dimeric sites have a strong tendency to reduce to less active, isolated Ga^+ ions. Continuous addition of water stabilizes these dimers. These improved reaction conditions were derived from state-of-the-art quantum-chemical calculations of the elementary reaction steps of alkane dehydrogenation (Figure D.13, left; alkane activation over $Ga_2O_2^{2+}$). In essence, the Ga/ZSM-5-water combination forms a self-repairing catalytic system for alkane dehydrogenation (Hensen et al. 2007).



Shell	R (Å)	CN
Ga-O	1.84	4.1
Ga-Ga	2.98	1.1
Ga-Al	2.72	1.1

Figure D.13. Alkane activation over $Ga_2O_2^{2+}$ (left). *In situ* X-ray absorption spectroscopy shows the predominant presence of Ga_2O_2 cations (right).

Development of a new hydrogen storage material with new generation NiMH batteries as potential application.

The group *Energy Materials and Devices* (Notten/Hintzen) focuses on three research themes all related to *Sustainable Energy Technologies*, i.e., (*i*) hydrogen storage to enable the future hydrogen economy, (*ii*) electricity storage in rechargeable batteries to power a wide range of applications, ranging from small autonomous (medical) devices to future plug-in hybrid cars and (*iii*) spectral conversion materials, making Si-based solar cells much more efficient.

One of the selected highlights deals with 3D-integrated all-solid-state batteries (see Figure D.14), which makes use of the extreme intercalation properties of Si. A recent publication, entitled "3D-integrated all-solid-state rechargeable batteries," (Notten et al. 2007) discloses a new concept, which was recently highlighted in an article in *Nature* (Armand and Tarascon 2008).

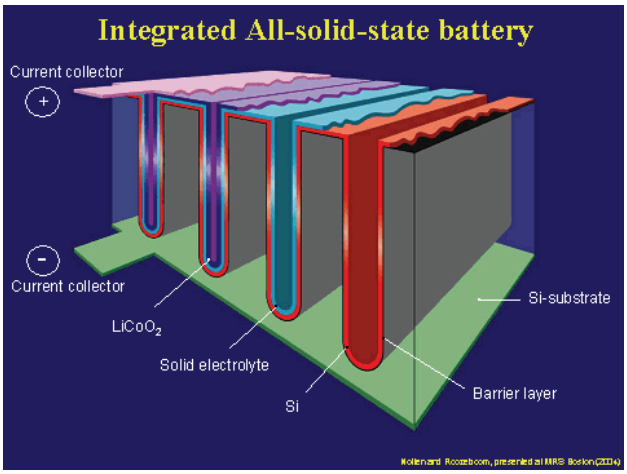


Figure D.14. Integrated all-solid-state battery.

SUMMARY AND CONCLUSIONS

Catalysis is a high-priority area for the Netherlands, and research at TU/e is highly coordinated and closely aligned with national and EU initiatives. The investment in catalysis research is substantial, partly as a

consequence of the influence of industry on government-funding priorities. The work has been of very high impact and the results have been disseminated via publications and important workshops (copies of some presentations were provided). As appropriate, the results of academic research are translated into products. It was mentioned that the WTEC panel should have considered visiting India, Singapore, and South Africa.

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BACKGROUND

The ETH Catalysis and Reaction Engineering Group currently has 1 research head (Alfons Baiker), 1 half-time secretary, 4 scientific staff, 13 post-doctoral researchers, and 13 PhD students. Approximately one-third of the students at ETH are Swiss with the majority of the others being from the EU. From 1995 to the time of the WTEC site visit, the research group had published 486 peer-reviewed journal publications.

A large portion of the funding for the Baiker Research Group comes from the university. A professorship at ETH comes with funding of other positions. The lead professor can decide on the job description of these positions. It is also possible to get SEED funding for high-risk projects from ETH. Instrumentation and equipment is provided from Swiss grants, ETH, and industry. In the past, up to 60% of the funding for research in this group was provided by industry, mainly in the field of applied catalysis. Presently, Prof. Baiker's group is focusing more on fundamental aspects of catalysis, which research is less supported by industry. ETH is also very interested in commercializing technology developed at ETH. Prof. Baiker says that patents are now probably even more appreciated than papers, from a university point of view.

There are three pillars of research in the Baiker research group:

1. New catalyst materials
2. *In situ* spectroscopy
3. Reaction engineering

Knowledge gained in these fields is applied to the design of catalytic systems for the synthesis of fine chemicals and for environmental catalysis.

RESEARCH AND DEVELOPMENT ACTIVITIES

Figure D.15 summarizes some of the major research areas in the Baiker group.

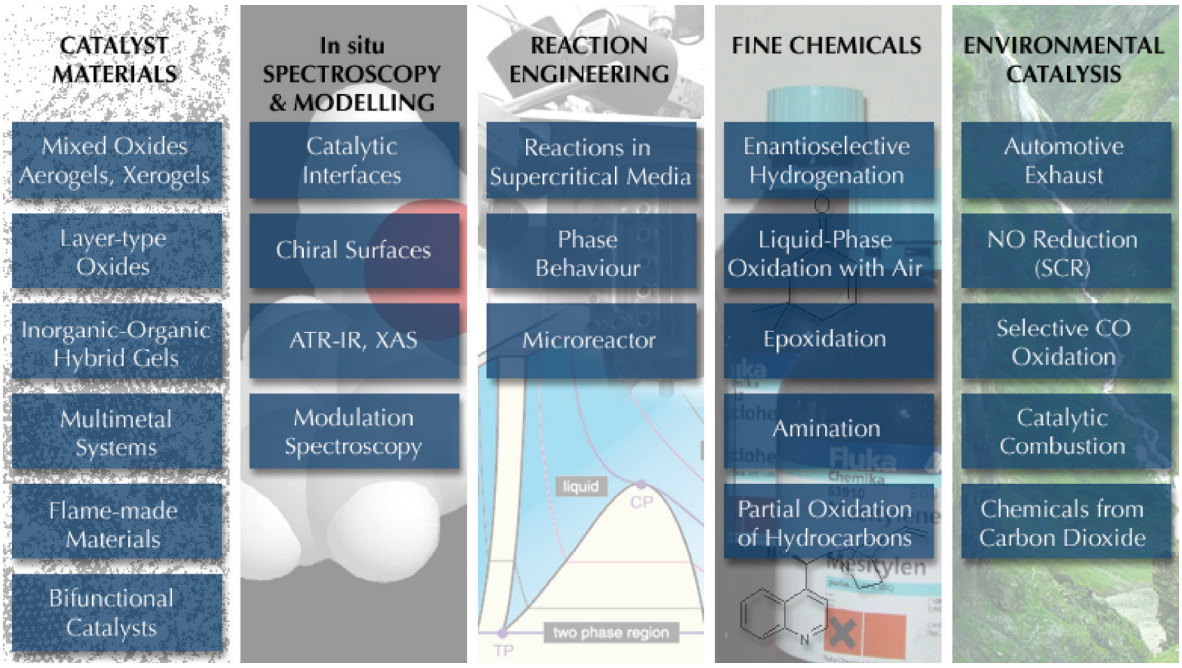

Figure D.15. Major research areas of the Baiker Research Group (courtesy of A. Baiker).

Fine Chemicals

The Baiker research group is a world leader in developing strategies for production of enantiomerically pure compounds with heterogeneous catalysts (Baiker 2005; Diezi et al. 2004; Mallat, Orglmeister, and Baiker 2007; and Vargas et al. 2007). This has application in the manufacturing of pharmaceuticals and fine chemicals. Baiker (2005) has estimated that in 2002 the revenues of the global chiral technology market were $7 billion and till 2009 they are estimated to grow to over $10 billion.

While the development of homogeneous enantioselective catalysis has received a tremendous amount of interest, culminating with the Noble Prizes in Chemistry of 2002 awarded to Knowles and Noyori, the same amount of interest in heterogeneous catalysis has not taken place. This is due to challenges with being able to create well-defined, catalytically active, and stable chiral sites on a solid surface (Baiker 2005). However, solid catalysts offer advantages due to their ease of separation, reuse, and regeneration. Furthermore, they provide interesting opportunities for the development of continuous chiral synthesis.

Figure D.16 demonstrates some of the strategies that are being used to create a chiral structure. One of the more obvious strategies is the immobilization of chiral transition metal complexes on a suitable support material. These immobilization techniques include impregnation, grafting, tethering, and encapsulation. Another approach is molecular chiral imprinting (which is *not* an approach that is being used in the Baiker group).

A third approach is the creation of chiral sites on metal surfaces, which is a major research area in the Baiker group. This can be done using two different approaches: (1) modification of the surface by adsorption of chiral organic compounds (modifiers), or (2) development of intrinsically chiral surfaces. The first of these approaches is probably the most promising method for development of chiral surfaces. The major limitation with intrinsically chiral surfaces is the low number density and structural stability of the chiral sites (Baiker 2005).

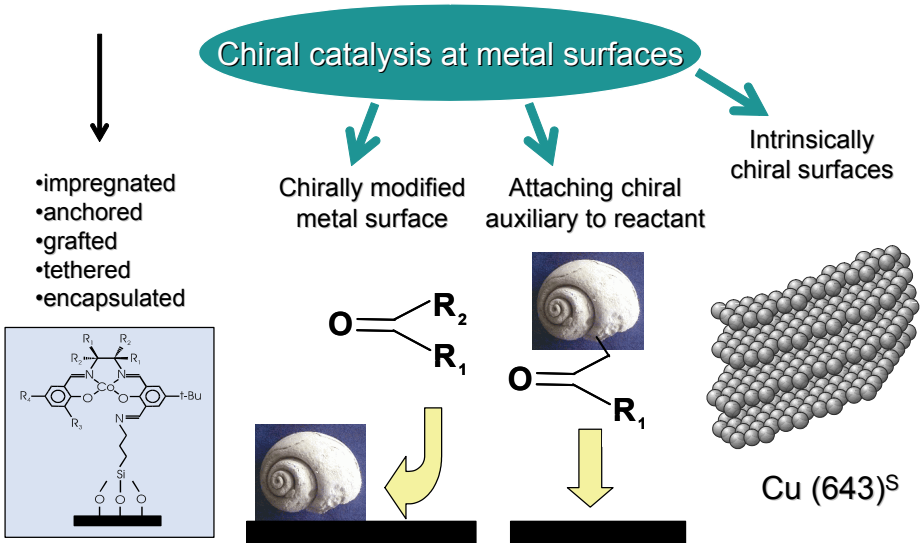

Figure D.16. Strategies for asymmetric heterogeneous catalysis (courtesy of A. Baiker).

One example of enantioselectivity with modified chiral surfaces that used theory, *in situ* spectroscopy, and experiments was the hydrogenation of ethyl pyruvate and other activated ketones, as shown in Figure D.17 (Vargas et al. 2007). Figure D.17 shows the modifier (cinchonidine and O-phenylcinchonidine) adsorbed on the Pt surface and how the Pt surface can become a chiral surface. These modified transition metal surfaces operate in ways that are analogous to those of enzymes. An orbital rich transition metal activates the reactant towards a transformation, and the flexible carbon skeleton of a modifier directs the reactant to adopt a specific orientation with respect to the surface that is ready to deliver adsorbed hydrogen.

Figure D.18 shows an example of a continuous reactor that can produce enantiomers by hydrogenation with chiral modified supported metal catalysts.

Other classes of catalytic reactions used in fine chemistry that are in the focus of the Baiker group are aerobic oxidations, epoxidations, and aminations.

In Situ Spectroscopy and Modeling

The Baiker research group has developed a variety of *in situ* spectroscopy techniques useful for the investigation of catalytic solid-liquid interfaces. The group uses also a variety of modeling techniques to complement the structural information gained by spectroscopy. During the WTEC team's visit, the techniques that we heard the most about were attenuated total reflection (ATR) (Figure D.19; Bürgi, Wirz, and Baiker 2003) and X-ray absorption spectroscopy (XAS) (Figure D.20; Grunwaldt 2003).

The Baiker group is developing a transient ATR method (that uses step changes in reactant concentration) that will allow detection of adsorbed species on supported metals catalysts. The researchers demonstrated that this method is able to differentiate between species involved in the catalytic process and spectator species. This will be a promising technique for detection of oxygenate species adsorbed on metal surfaces, because these species are hard to detect since they also adsorb on the support. The Baiker research group has also developed a number of *in situ* techniques that are useful for studying reactions under demanding conditions, including under supercritical conditions and high pressure.

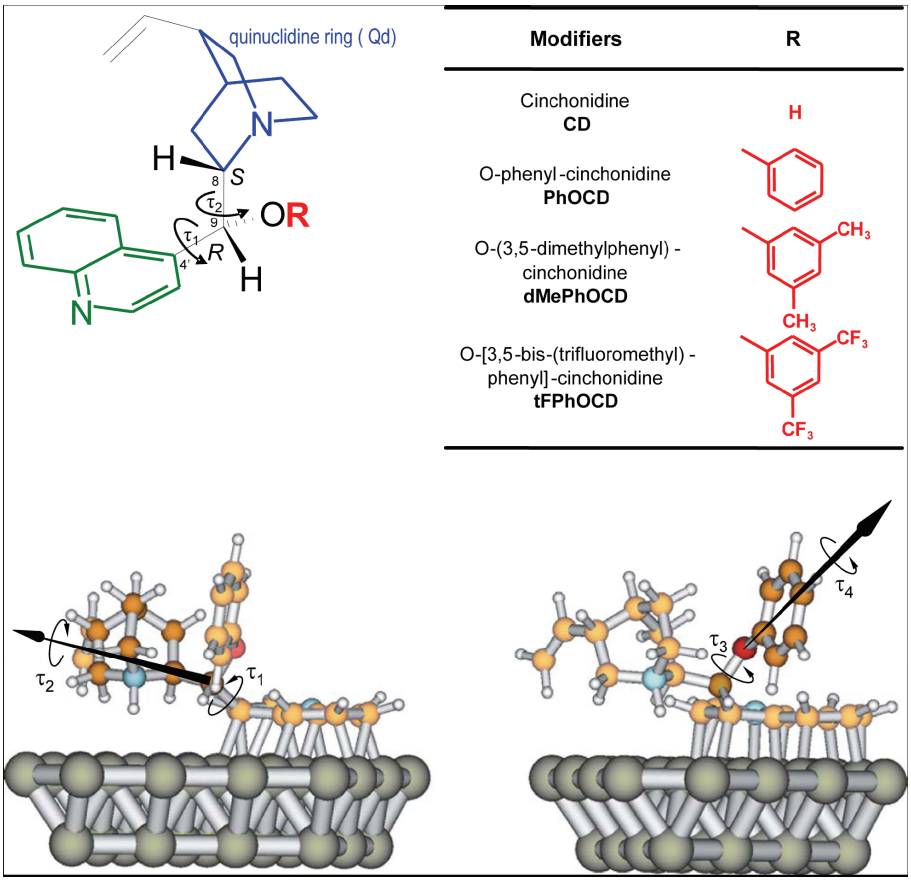

Figure D.17. Top: Chemical structures of cinchona-alkaloid modifiers with the main submolecular moieties at C8 and C9. Bottom: Two views of a stable conformer of PhOCD adsorbed on platinum. This figure demonstrates how changes in the structure of the modifier can be used to change the enantioselectivity for hydrogenation of ethyl pyruvate (reprinted with permission from Vargas et al. 2007).

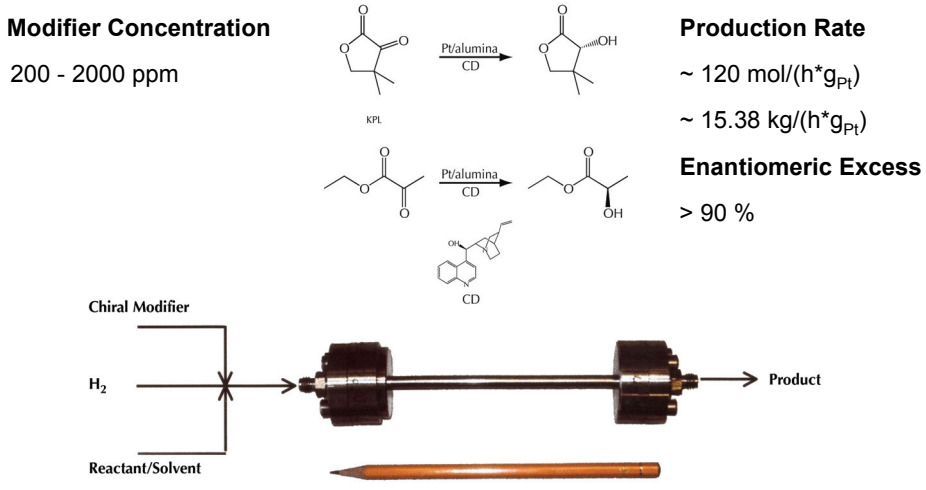

Figure D.18. Continuous process for efficient hydrogenation of ketocarbonyl compounds (courtesy of A. Baiker).

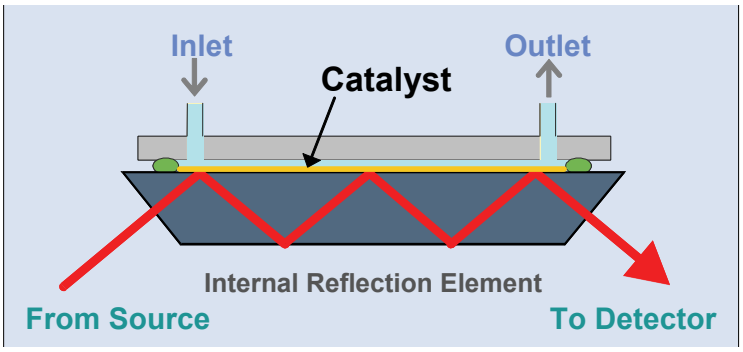

Figure D.19. Attenuated total reflectance IR cell (courtesy of A. Baiker).

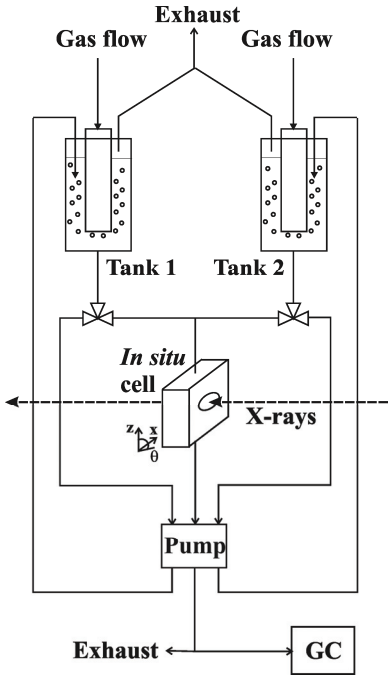

Figure D.20. Schematic of *in situ* X-ray absorption spectroscopy (XAS) cell (reprinted with permission from Grunwaldt et al. 2003).

Catalyst Materials

The Baiker group studies a range of catalytic materials, including flame-made materials (supports and metal-supported catalysts), bifunctional catalysts, layer-type oxides, inorganic-organic hybrid gels, chiral inorganic materials (described in the previous section) and multimetal systems. The WTEC team saw flame synthesis preparation of bimetallic supported catalysts. The process of flame synthesis of compounds is shown schematically in Figure D.21 (left side) for the production of Pt-Rh/Al_2O_3 catalysts for partial oxidation of methane (Hannemann et al. 2007).

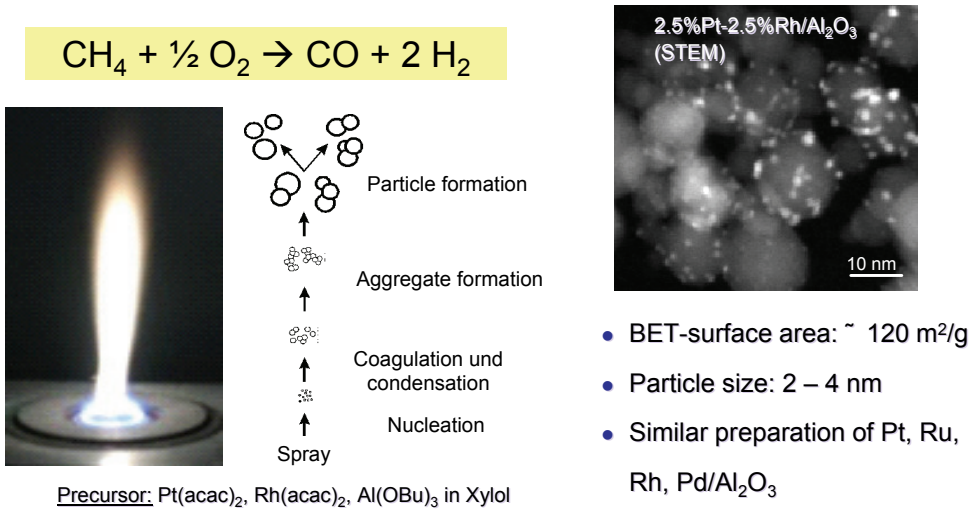

Figure D.21. Pt-Rh/Al_2O_3 catalyst for the partial oxidation of methane prepared by flame synthesis (courtesy of A. Baiker).

Reactions in Supercritical Fluids

Another major research thrust of the Baiker group is studying reactions in supercritical fluids (Grunwaldt et al. 2003; Seki, Grunwaldt, and Baiker 2007). Some potential advantages of supercritical fluids are an increase in reaction rates and the ease of separating catalysts and reactants after reaction. Figure D.22 shows one example of a reaction in supercritical fluid and how the reaction rate increases as the reactor pressure increases. The group has a range of supercritical reactors, including a continuous flow supercritical reactor and several that have *in situ* techniques, as shown in Figure D.23.

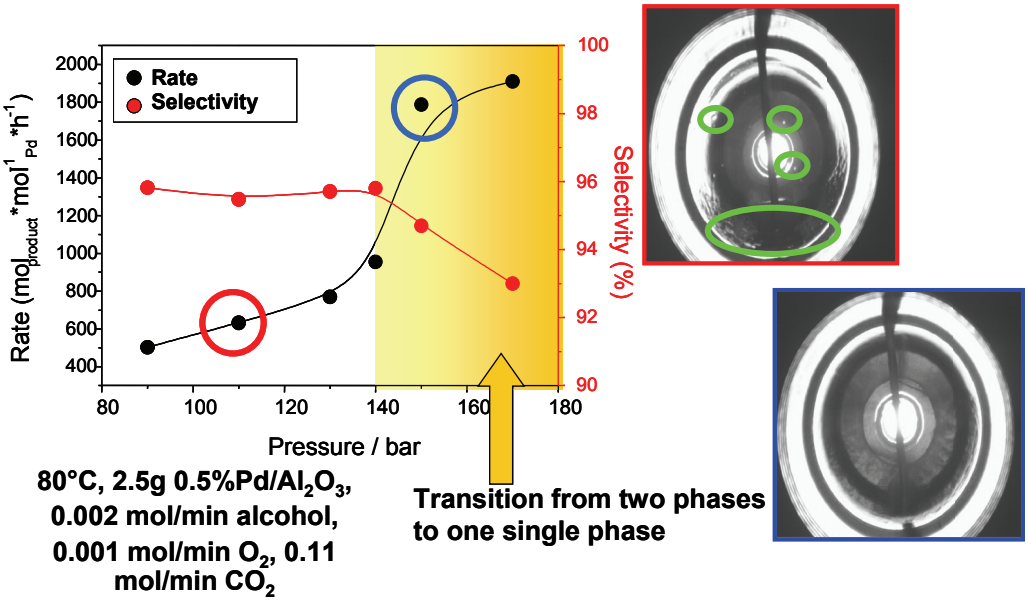

Figure D.22. Influence of pressure on reaction rate and selectivity for oxidation of benzyl alcohol. The figure and pictures show the transition from two phases to one-single phase. The circles in green show droplet formation indicating two phases (reprinted in part with permission from Caravati et al. 2005).

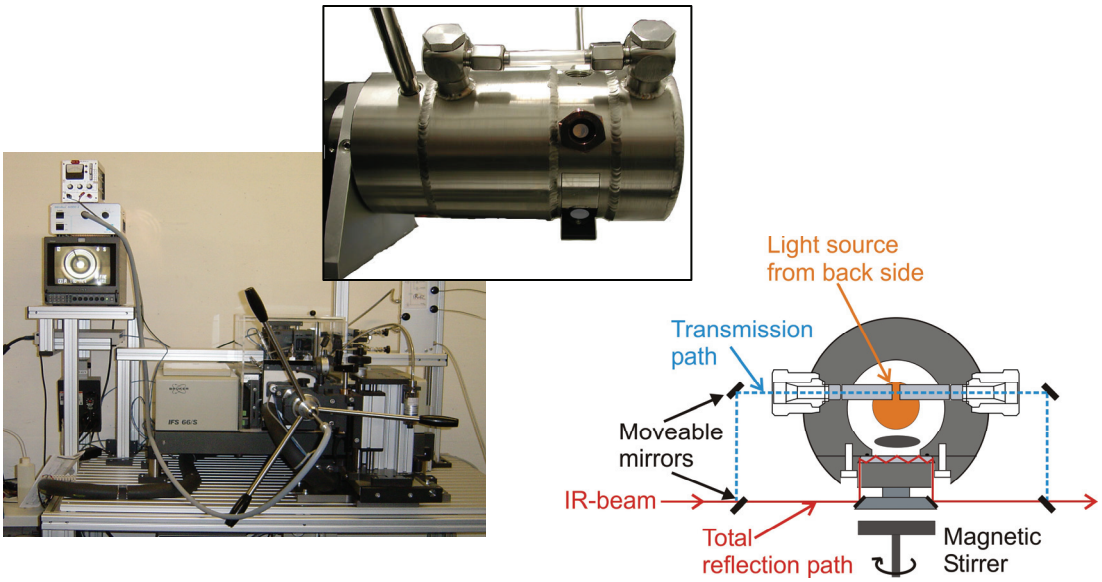

Figure D.23. Supercritical reactor with view cell and *in situ* transmission and ATR-IR (reprinted in part with permission from Grunwaldt and Baiker 2005).

Currently also in the focus of the Baiker group are microreactors that can be used with supercritical CO_2, as shown in Figure D.24.

Figure D.24. Reactions in supercritical CO_2 in a microreactor (courtesy of Ph. von Rohr, ETH).

Environmental Catalysis

The main present activities of the Baiker group in environmental catalysis embrace the use of CO_2 as a C-1 building block in the catalytic synthesis of various chemicals, automotive exhaust catalysis and catalytic combustion. In the area of automotive catalysis, the focus is on NO_x storage-reduction catalysts in cooperation with industry. New materials are developed for NSR and fundamental insight into the storage and reduction process is gained by space- and time-resolved vibrational spectroscopies (Urakawa Maeda, and Baiker 2008).

SUMMARY AND CONCLUSIONS

The strengths of the Baiker research group are in chiral metallic surfaces, supercritical reactions, development of *in situ* spectroscopy under demanding reaction conditions, oxidation catalysis, $DeNO_x$ catalysis, and sol-gel and flame synthesis of catalytic materials. The support from ETH and several

governmental and private foundations of Switzerland that is provided to the Baiker research group allows the development of long-term research projects that can focus on the fundamental scientific questions relevant to catalysis and provide instrumentation that is world-class.

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BACKGROUND

The Fritz Haber Institute (FHI), founded in 1911, was originally known as the Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry and included the Kaiser Wilhelm Institute for Chemistry. Although the Kaiser Wilhelm Society partially financed the institute, it was set up under a generous endowment by Leopold Koppel, a wealthy industrialist and banker, to be governed by an endowment council, a scientific board, and a director. Fritz Haber was the first director of the institute. Its focus was basic research in physical chemistry to support the German chemical industry, commonly regarded as a world leader at the time.

After the start of World War I, the focus of the institute shifted toward subjects of military interest such as explosives and chemical weapons. In 1918, Haber was awarded the Nobel Prize in Chemistry for his work on ammonia synthesis. New departments in Colloidal Chemistry and Atomic Physics were established and directed by notable scientists H. Freundlich and J. Franck, and a new Department of Physical Chemistry was opened under the leadership of M. Polanyi. The institute was host to many prominent young scientists of the era. The rise of the National Socialists in Germany after World War I severely affected the Institute. Fritz Haber resigned as director in 1933 along with department heads Freundlich and Polanyi, followed later by many of the staff scientists. During World War II, the institute once again focused almost exclusively on military projects. Under the direction of Max von Laue, the institute was officially incorporated into the Max Planck Society in 1953 as the Fritz Haber Institute.

The transformation of the institute into a center of excellence in catalysis and surface reactivity began in the late 1950s under the direction of Rudolf Brill, who was particularly interested in catalysts used for ammonia synthesis, hydrogenation, and oxidation. After periods of restructuring in the 1970s and 1980s, research involving spectroscopy and chemisorption on solid surfaces gained prominence at the institute. The institute was also heavily involved at that time with the planning and administration of BESSY, a synchrotron radiation light source in Berlin. In 1985, Gerhardt Ertl's appointment as Director of Physical Chemistry increased the focus on structure and chemical reactions on solid surfaces. In 1988, a theory department was formed, which specialized in surface theory as well as solid-state research, quantum chemistry, and computational physics. In 1994, a new Department of Inorganic Chemistry began to focus efforts toward heterogeneous reactions on inorganic surfaces. The scientists at the FHI continued to be highly regarded by the world scientific community. Ernst Ruska was awarded the Nobel Prize in 1986 for his work at the FHI on the development of electron microscopy.

In 1995 Hans-Joachim Freund was appointed director of the Department of Surface Reactions, which has since been renamed the Department of Chemical Physics. The focus of the department under Freund's direction involves adsorption and reaction on model solid oxide surfaces. Gerard Meijer was appointed in 2002 as director of the Department of Molecular Physics and currently serves as the overall director of the Fritz Haber Institute.

The institute currently has a focus on catalysis as well as on chemical and physical properties of surfaces, interfaces, molecules, clusters, and nanostructures. According to the 2005 report for its external advisory board, the institute has 42 positions, 24 of which are for tenured scientists. There are 5 director positions and 148 technical staff positions. Normally, the institute employs 80–100 PhD students, although many are supported by outside funding. Thus, the institute can be generally described as 5 independent departments (Inorganic Chemistry, Chemical Physics, Molecular Physics, Physical Chemistry, and Theory), each with about 50–60 people. In addition to technical and research staff, the FHI has excellent support staff in computer services (~5), electronics (~15), and mechanical workshops (~15).

The budget for the institute is quite stable after a new method of financial planning was adopted by the Max Planck Society in 2004. Now the institute receives annual and fixed core budgets that allow for increases due to inflation. The annual budget at the FHI for personnel was ~€12–13 million over the period 1997–2007, whereas the total institute budget was about twice that value. The majority of the funding (~60%) is derived from the Max Planck Society; other sources such as the German Science Foundation, the European Union, and individual grants and fellowships provide the remaining 40% of funds. Since most of the research at the institute is fundamental in nature, less than 5% of the budget is derived from industrial sources. Long-term stability of the budget was emphasized to the WTEC visiting team as a major reason why researchers at the FHI can accomplish scientific goals beyond those typically pursued in U.S. academic laboratories. Moreover, the extensive use of research technicians is critical to the construction of complex machines that are beyond the skill sets of graduate students and postdoctoral researchers. The Fritz Haber Institute is ranked first among non-university organizations for international Humboldt fellows.

The success of the institute is determined primarily by a panel of experts who visit every two years to evaluate the programs. The placement of graduate students and postdoctoral researchers in desirable research and faculty positions is part of the evaluation criteria. Although publication of research papers is important, it is not a sole measure of success. This perspective on scientific success appears to be unique in Europe and was certainly unique among the sites visited by the WTEC panel.

RESEARCH AND DEVELOPMENT

The visiting team met with Professors Gerard Meijer, Hajo Freund, and Robert Schlögl, and Dr. Kartsen Reuter. Since the laboratories of Prof. Schlögl were temporarily located away from the FHI because of building renovations, the visiting team toured only the labs of Professors Meijer and Freund.

Department of Molecular Physics

As the current director of the Fritz Haber Institute, Professor Meijer graciously provided an overview of the entire facility as well as a personal tour of his department. Meijer moved his laboratory to the Fritz Haber Institute from the FOM Institute for Plasma Physics in Nieuwegein, The Netherlands, in late 2003.

The main focus of the laboratory is to control molecules in the gas phase to allow for fundamental investigations of molecular properties. A major tool is a free electron laser that is used to provide a tunable source of infrared radiation. An interesting feature of the laboratory is that the laser lab is in a separate temperature-controlled room with periscopes to move the beams into the machine room.

In one experiment, laser ablation of vanadium atoms in the presence of argon is followed by cooling to liquid helium temperatures to produce charged gas phase clusters of V with 1 Ar atom attached. Irradiation of the $(V_xAr)^+$ clusters with IR photons is used to excite internal modes of the cluster, which subsequently leads to dissociation of the weak V_x^+ bond to Ar. Since the absorption of IR photons depends sensitively on the

number and arrangement of V atoms in the cluster, the dissociation of Ar from the cluster is a good measure of the cluster size. For example, a $(V_7Ar)^+$ cluster will absorb specific frequencies of IR radiation to give dissociated V_7^+ and Ar fragments. Thus, absorption of the IR photons will result in a loss in the mass spectrum of the gas phase clusters associated with the $(V_7Ar)^+$. By combining mass spectrometry and IR irradiation, a depletion spectrum can be derived that is related to the IR spectrum of the individual clusters. Comparison of spectra to those predicted by density functional theory can be used to postulate structures of the vanadium clusters (Ratsch et al. 2005). This technique can be used to evaluate the IR "absorption" spectrum of individual clusters of species relevant to catalysis such as CO bound to Rh or Au metal clusters.

A separate line of inquiry in the lab involves the characterization of low energy neutral molecules. Meijer has constructed a series of linear decelerators based on the Stark effect associated with a dipole moment in a molecule. In a Stark decelerator, 10^6 molecules can be prepared in a single pulse to have a single quantum state and orientation for as long as one second. Figure D.25 shows a decelerator constructed at the Fritz Haber Institute. Meijer emphasized that research engineers constructed the electrode assemblies for the decelerators because students and postdocs could not carry out this type of precision work. Additional information on the investigation of decelerated OH radicals can be found in Meerakker et al. (2005).

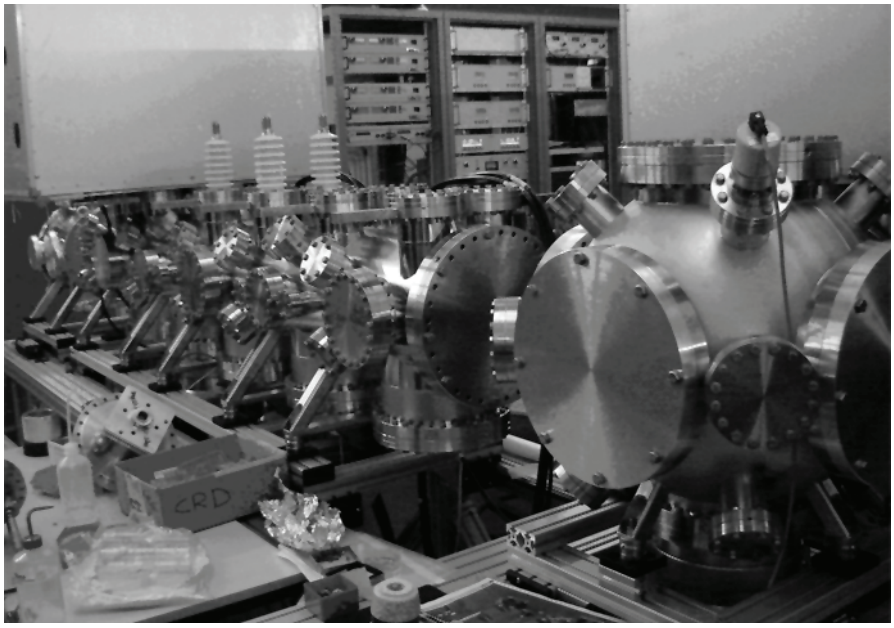

Figure D.25. Stark decelerator in the laboratory of Prof. Gerard Meijer (photo courtesy of FHI, H.-J. Freund).

Department of Chemical Physics

The second laboratory tour was hosted by Professor Hajo Freund. His department is staffed with 65 people and is focused on oxide surfaces and the interaction of both metal and metal oxide nanoparticles on surfaces. The lab is outfitted with 25 ultrahigh-vacuum machines, each with multiple analysis techniques. The staff is divided into nine working groups: (1) Spectroscopy and Spectromicroscopy, (2) Structure and Reactivity, (3) Low-Temperature STM, (4) Scanning Probe Spectroscopy, (5) Magnetic Resonance, (6) Catalysis/Laser Spectroscopy, (7) Molecular Beam, (8) Photon-Induced Processes, and (9) Theory. A detailed review of the successes of these groups is beyond the scope of this report.

To summarize the lab's activities, 10 people in two groups are heavily involved with the synthesis of model systems such as thin-film oxides. Two other groups are involved with doing chemistry on those surfaces by molecular beam techniques and in high-pressure conditions. Recent topics of study are preparation of ultrathin-film silica; characterization of color center defects on MgO(100) films; investigation of Au, Ag, and AuAg alloy nanoparticles on a variety of supports; exploration of Pd particle size effects in hydrogenation

catalysis; oxidation of Pd nanoparticles on iron oxide; characterization of supported vanadia, silica, and alumina particles; and photochemistry of molecules on supported Ag nanoparticles. Characterization is accomplished not only by standard surface science methods, but also by nonlinear optical techniques such as sum frequency generation and polarization-modulated-FT-IR spectroscopy. The photochemistry experiments on Ag utilize a new apparatus combining resonant multiphoton ionization techniques with two-photon photoemission spectroscopy. Moreover, characterization of plasmon resonances associated with Au and Ag particles is accomplished by using a home-built photon STM, which utilizes an STM apparatus to excite photons from the sample.

A significant effort in the group is involved with pushing the limits of experimental techniques by continually developing new instrumentation. The department is currently developing an ultrahigh-resolution spectromicroscope (known as SMART), a high-field W-band electron paramagnetic resonance spectrometer to investigate surfaces in ultrahigh vacuum, and a new low-temperature STM. The SMART utilizes both chromatic and spherical aberration corrections to overcome the resolution limitations of currently available photoelectron emission microscopes (PEEM) to give a projected lateral resolution of 2 nm and an energy resolution of 100 meV, which is claimed to be the most ambitious project in the field of spectroscopic microscopy in the world. In addition to performing photoemission spectroscopy (PEEM, XPEEM, LEEM), the tool can also be used for NEXAFS, XPS, and Auger spectroscopy as well as for diffraction methods such as micro-spot-LEED and PED.

The development of electron paramagnetic resonance for characterization of surfaces in ultrahigh vacuum has been a hallmark of the group for many years. A current goal is to accommodate a 95 GHz spectrometer with a UHV chamber to provide enhanced spectral resolution and intrinsic sensitivity over their existing 10 GHz instrument. Moreover, pulse spectroscopic methods will now be possible with the new instrument. This instrument adapted for use with surfaces in UHV is unique in the world. Figure 3.6 shows the tool under development. By combining low-temperature STM with photon STM, the group hopes to record Auger spectra with nearly atomic resolution.

One goal of future work will involve the use of STM in liquid water to study how metal salts bind to surfaces during catalyst preparation. Questions such as “How do metals lose their ligand sphere?” and “How do metals anchor to surfaces?” during wet preparation methods will be addressed by these future studies. The reader is referred to the report to the Fachbeirat (FHI 2005) for a list of recent publications from the laboratory and detailed descriptions of the ongoing research topics.

Department of Inorganic Chemistry

Although the laboratories of this department could not be toured during the WTEC team’s short visit, the panel was fortunate to have a discussion with the director, Professor Robert Schlögl. The department, which is staffed with about 60 people, is searching for the scientific origins of the pressure gap and materials gap that exist between surface science and catalysis. The department is composed of four groups that focus on different aspects of catalysis, including (1) Preparation, (2) Functional Characterization, (3) Surface Analysis, and (4) Microstructure. Approximately 15 people are dedicated to liquid-solid synthesis of catalysts at a moderate scale (~100 g batches). Prof. Schlögl indicated that catalysts prepared on the 100 g scale are more reproducible than those produced on a smaller scale. The suit of characterization tools available to the different groups is very impressive and consists of

- spectroscopic methods: Raman (5 wavelengths available), *in situ* UV-Vis-NIR (2 units), *in situ* IR (4 spectrometers with DRIFTS and transmission capability)
- *in situ* photoelectron and synchrotron radiation methods
- chemical and physical tools: elemental analysis, *in situ* XRD, TG, variable atmosphere DSC, calorimetry (4 units), adsorption, TPD, TPR, TEM (3 microscopes), and SEM (2 microscopes)

The Inorganic Chemistry Department has the most industrial collaborations in the FHI. Industrial projects deal with catalysts for methanol synthesis, propane oxidation, ammonia synthesis, ammonia decomposition (for H_2 generation), and carbon synthesis. Other topics in the lab involve important reactions such as dehydrogenation of ethylbenzene to styrene over iron oxide or nanocarbon materials, alkane isomerization on

sulfated zirconia, butane oxidation to maleic anhydride over vanadia, alkyne hydrogenation to alkene over palladium, and selective hydrogenation and oxidation reactions over silver.

Discussions with Professor Schlögl about the future of the Department of Inorganic Chemistry were quite informative. His direct observation that catalysts restructure under reaction conditions has led him to postulate that perhaps many or all active catalysts undergo a dynamical cycle of surface restructuring that is on the same time scale as the turnover cycle of a catalytic reaction. Thus, he is exploring the dynamic feedback loops that exist between the gas phase (composition, temperature, and pressure) and the structure of the reactive surface. Ongoing work in his group is also exploring the use of non-oxide solids for oxidation reactions. The visiting team was particularly impressed by the development of *in situ* XPS capabilities. Prof. Schlögl indicated the instrument is a critical tool that is located at a BESSY beamline and allows for photoemission experiments to be performed on samples exposed to gases up to 10 mbar. The instrument was developed in collaboration with M. Salmeron at the Lawrence Berkeley Lab over a period of 10 years, illustrating again the importance of sustainable funding over a long period of time.

Department of Theory

The Theory group, which is directed by Professor Matthius Scheffler, has 6 group leaders, 33 graduate students, and over 34 guest scientists. This group is one of the leading groups in the world in theoretical and computational materials science. The focus of the group is on understanding the fundamental chemical and physical processes that occur on surfaces, interfaces, and nanostructures. The department maintains a strong emphasis on catalysis and processes related to catalysis. Most of the work in catalysis is codirected by Dr. Karsten Reuter, who was appointed by the Max Plank Society as an Independent Junior Research Group Leader in the area titled First Principles Statistical Mechanics. The group's current focus is aimed at the theme "Beyond DFT" whereby more accurate *ab initio* treatments are being developed for surface chemistry. Thus, group scientists are developing more accurate theoretical methods to treat reactive surfaces, including (1) "exact-exchange" to improve on current functionals within density functional theory, (2) development of an all-electron GW approach, (3) development of a more computationally efficient and accurate GW pseudopotential code that can more accurately calculate the excitation spectrum from surfaces, and (4) more accurate total energy calculations by combining DFT surface calculations with advanced Møller Plesset Perturbation theory or couple cluster methods.

Over the past few years Theory Department scientists have also been developing a New Atom Centered Basis Set Code. Use of atom-centered basis sets rather than the more traditional planewaves for surfaces offers significant advantages in CPU time, memory, scaling, and the treatment of nonperiodic systems. In addition, the group has pioneered the development of *ab initio* thermodynamics and statistical mechanics to establish the thermodynamically most favorable surface structures and compositions that may form under reaction conditions. While the group's focus has been on the state of the working metal surface under oxidizing conditions and the application to CO oxidation, its approach is now being used by the entire theoretical surface science community. The group is also developing and using *ab initio*-based kinetic Monte Carlo simulations to integrate the fundamental kinetics established from theory and statistical thermodynamics to more accurately describe the microscopic and macroscopic catalytic kinetics. Its current efforts have been focused on using the simulations to provide a sensitivity analysis of the most important kinetic processes for CO oxidation. Group members have also been working on understanding the catalytic properties of metal clusters and the behavior of chiral molecules on surfaces.

Department of Physical Chemistry

Prof. Meijer is the acting director of the Department of Physical Chemistry until a replacement is found for Gerhard Ertl, who retired in 2004. The panel did not tour the laboratory but recognized its history in the experimental and theoretical studies of nonlinear dynamical phenomena in various interfacial reactions. Soon after our visit, Professor Ertl was awarded the 2007 Nobel Prize in Chemistry for his pioneering work on surface reactivity. The Physical Chemistry Department under Professor Ertl's direction had a tremendous impact on the field of kinetics of elementary surface reactions.

SUMMARY AND CONCLUSIONS

The Fritz Haber Institute is a very impressive research organization that is unique in the world. With its outstanding scientific leadership, sustained level of funding, special evaluation process, extensive utilization of expert research technicians, and collaboration with doctoral and postdoctoral students, the Fritz Haber Institute is able to accomplish fundamental research in catalysis and surface science that determines the state of the art worldwide. The scientific directions at the institute are set by the directors of the departments, not by the central administration. The facility attracts applications from students and postdoctoral researchers from around the world, which allows the directors to be extremely selective in the admission process. About 40–50% of the students and postdocs are from Germany. The track record of this institute is excellent, and it will likely be a major player in catalysis and surface science research for the foreseeable future.

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Date Visited: September 27, 2007

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BACKGROUND

Founded in 1940 by Dr. Haldor Topsøe, Haldor Topsøe A/S is an international chemical company with offices in the United States (Los Angeles, Houston), Russia (Moscow), United Arab Emirates (Bahrain), China (Beijing), Japan (Tokyo), India (Delhi), and Argentina (Buenos Aires), with their head office and main R&D facilities in Lyngby, Denmark. It is a catalysis and technology company with an annual turnover of $800 million. It has research collaborations with leading universities worldwide and is open for scientific and technology research.

The company currently has 1800 employees, of whom approximately 280 employed in the research and development division. The three major divisions within the company are (1) Topsøe Catalysts, (2) Topsøe Technologies, (3) Topsøe Research and Development. In addition, a subsidiary, Topsøe Fuel Cells (TOFC), has been established. General activities of the company can be divided into (1) R&D in heterogeneous catalysis, materials science and reaction engineering, (2) catalyst production and sales, (3) licensing of technology, and (4) equipment supply.

RESEARCH AND DEVELOPMENT

During the site visit, the WTEC panel met with Dr. Nerlov and Mr. Dibbern, who provided an overview of the company and current research interests. Company activities can be divided into following general themes:

- Materials and preparation
- Characterization and analysis
- Catalysis and processing
- Reactions and process models

Research efforts are multidisciplinary and cover the entire spectrum, including fundamental research (including computer modeling and theory), catalyst development, manufacturing, process development and impact, and pilot plants studies. The Topsøe group currently has collaborations with 11 universities and 5 research institutes. It also has 7 professors from 6 universities and 4 independent consultants. The Topsøe catalyst forum is a venue for exchange of ideas and know-how with leading scientists on selected topics relevant to the company. The company has strong connections with the Technical University of Denmark (DTU), and it sponsors research programs as well as shares PhD students, either via direct funding or internship programs.

The research projects undertaken must have a well-defined target, relevance for Haldor Topsøe business, a possible sponsor in the commercial divisions, a reasonable time horizon, well-defined milestones, criteria for

go/no-go decisions, available resources, and required competencies. Various research groups are working on syn gas production and conversion, coal gas conversion, hydrotreating, hydrocracking, $DeNO_x$, and automotive exhaust catalysts.

Characterization and analysis activities at the R&D division rely heavily on understanding the dynamic processes happening under reaction conditions using various *in situ* techniques such as QEXAFS, XRD, Laser Raman, ESR, and ETEM. Most of the facilities, including a 12-server dual processor for DFT calculations, are located at the Lyngby facilities, but Haldor researchers also use facilities at DTU and the synchrotron facilities at Hamburg.

Figure 4.9 (Chapter 4) shows the effect of environment on the structure and morphology of Cu catalyst on ZnO support during reduction. *In situ* observations of the process revealed that the shape of the particles depended on the reducing environment. For example, the particles were observed to be faceted with their (111) planes in contact with the support in H_2 atmosphere (Figure 4.9, A and B). Addition of water to H_2 (mild reducing environment) resulted in more round-shaped particles terminated by (110) and (100) planes, but the contact area with the support remained unchanged (Figure 4.9, C and D). On the other hand, a more reducing environment obtained by replacing H_2O by CO, had a more pronounced effect on the morphology and increased wetting area to the support (Figure 4.9, E and F). A detailed analysis of the structure and morphology was used to obtain surface energies and work of adhesion. Haldor Topsøe researchers also employ tomography to elucidate the location of catalyst particles with respect to the support. For example, 3D images obtained from a tilt series are used to determine whether the particles are on the surface or embedded in the support.

The solid oxide fuel cell subsidiary (TOFC) is developing a cell of 1-5 kW stack module with thin layers of cheap materials for household applications operating at 750°C with a target of 1kW/liter. The company has also introduced new generations of hydrotreating catalyst, named BRIM™ Technology. Development of these catalysts was aided by input from molecular-scale research; examples of these catalysts are TK-558 (CoMo) and TK-559 (NiMo) BRIM™ for FCC P/T and TK-576 BRIM™ (CoMo) for ULSD.

The WTEC panelists also had a chance to visit some of Haldor Topsøe's advanced labs, especially its world-famous transmission electron microscopy facilities (ETEM and ESEM).

SUMMARY AND CONCLUSIONS

Haldor Topsøe has a very strong basic research component within its R&D program. Although its researchers are involved in all aspects of catalytic research, there is strong emphasis on nanoscale characterization of catalysts in their reactive environments (*in situ*) using both spectroscopic (e.g., EXAFS) and imaging (ESEM and ETEM) techniques. Basic research is performed either in-house or by funding collaborative efforts at academic institutes. The company usually has 3–5 employees enrolled in PhD programs, and it supports approximately 10 PhD students at various universities. Intellectual property generally belongs to the company, but sometimes negotiations with academic partners can be lengthy and take 1–2 years.

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Date Visited: September 25, 2007

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BACKGROUND

The WTEC panel members met with Professors Di Renzo, Coq, and Goursot of the Laboratory for Advanced Materials for Catalysis and Healthcare (MACS) research team, which is one of eight independently financed research teams comprising l'Institut Charles Gerhardt Montpellier (ICGM). ICGM is a joint laboratory (UMR 5253) of several prestigious research organizations, namely Centre National de la Recherche Scientifique (CNRS), Université Montpellier 2 (Sciences), l'École Nationale Supérieure de Chimie de Montpellier (ENSCM, School of Chemistry), and Université Montpellier 1 (Medicine). ICGM is organized around 7 technical platforms jointly financed by the ICGM and Institut Européen de Membranes (IEM): XRD; NMR; magnetic methods (SQUID, EPR); IR and Raman; microscopies (SEM, TEM, AFM); dispersed solids (volumetry, thermal analysis, etc.); and polymeric materials. Moreover, the institute staff members have easy access to synchrotron radiation in Grenoble. It is a successful example of a research organization in France where academic and government research is virtually superimposed. CNRS plays a special role in this organization by not only providing research funding (similar to NSF in the United States), but also research staff for joint CNRS-university laboratories.

The origins of the MACS research team may be traced back to the "Laboratoire de Chimie Organique Physique Appliquée" created in 1970 by Professor Patrick Geneste at the School of Chemistry. Merging of specialists from heterogeneous catalysis and organic chemistry in the early 1980s led to new research directions and a new name: "Laboratoire de Chimie Organique Physique et Cinétique Chimique Appliquée." This laboratory was headed by Professor Geneste until 1994. François Fajula (Senior scientist from CNRS) became the head of the laboratory in 1995, which was then re-named as "Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique" or MACS. Since January of 2003, MACS has been headed by Dr. Bernard Coq (senior scientist from CNRS).

MACS is organized internally into four research groups:

1. Catalysis for Sustainable Development
2. Characterization of Advanced Functional Materials
3. Nanostructured Materials for Healthcare
4. Quantitative and Spectroscopic Approaches to Materials and their Functions

MACS is home to 15 CNRS researchers, 12 university teachers, 9 postdoctoral researchers, 15 graduate students, 13 technical staff and 3 administrative staff. Recent graduate students were mostly French (83%),

the remainder coming from Algeria (7%) and Bulgaria, Mexico, and Russia (3% each). The level of satisfaction with the qualifications of these students is decreasing as scientific careers become economically less appealing by comparison with other activities. In recent years, postdoctoral researchers came from France (37%), Romania (19%), India, Germany and Spain (~7% each), China, Morocco, Turkey, and the UK (~4% each).

MACS occupies 2300 m^2 of space in two locations in Montpellier: its own ENSCM laboratory and Faculty of Pharmacy at Université Montpellier 1 (Medicine). The current annual budget of the MACS laboratory (€3,450,000) includes staff salaries (CNRS, €2,500,000), other public funding (ANR, €400,000), European Union funding (€120,000) and industrial funding (€430,000). The success rate of competitive proposals submitted for government funding is ca. 15%, which much higher than the national average of ca. 3%.

Intellectual property resulting from industrially sponsored research is usually co-owned by CNRS and the industrial partner. The industrial partner in most cases buys out the CNRS rights to inventions, pays for filing patents which are typically expanded to WO level and cover most significant countries. The institute, including individual inventors and their laboratories, receives financial compensation for patented inventions only when a patent is successfully exploited. Although filing of patents is officially encouraged, a publication in an international journal receives more recognition.

MACS is actively engaged in international collaborations in the areas of catalyst testing (I. Ivanova, Moscow), IR spectroscopy of surface probe molecules (E. Garrone, Torino), *in situ* EPR studies of catalyst synthesis employing probe molecules (F. Ottaviani, Urbino), hyperpolarized ^{129}Xe NMR characterization of porosity (A. Gédéon, Paris), and metal replicas for the characterization of mesoporous materials (R. Ryoo, Seoul). Future plans involve developing collaborations in areas of *operando* characterization of catalytic systems, e.g., reaction SAXS and thermal analysis, and biological systems relevant to exploitation of renewable resources.

RESEARCH AND DEVELOPMENT

From the beginning, the MACS laboratory was fully involved in heterogeneous catalysis research through the design of catalytic materials and reactivity. On the one hand, MACS team is addressing the challenging aspect of the nanoscale description of the active site and its response to changing (*operando*) reaction conditions. On the other hand, a heterogeneous catalyst is a functional material dedicated to perform a reaction on a realistic scale. The basic research strategy of the laboratory is defined by these two aspects through an integrated approach to catalysis research. This is achieved thanks to the complementarities between the four research groups sharing skills in chemistry and physical chemistry of solids, organic chemistry, fine chemicals synthesis, kinetics, quantum chemical modeling, and spectroscopy, with strong relationships with industry.

At present, detailed description of functional catalytic materials in the areas of great societal concern, i.e., environment, energy, and health, is at the core of MACS research interests. Environmental catalysis at MACS deals with prevention of pollution through the design of highly selective chiral catalysts, clean processes (multifunctional catalysts), as well as pollution remediation (e.g., deNO_x). Research activities in the area of energy are related to refining (e.g., reformulated fuel and post-Fisher-Tropsch).

Research in the field of materials for life sciences deals with micro- and nano-encapsulation and controlled drug release employing porous materials. At the core of this research are (i) the self-assembly of nano- and mesostructured materials from ions, molecules and supramolecular entities, and (ii) the control of organic/inorganic interfaces. A key point for the design of these materials is the basic knowledge of the interfacial coordination chemistry: physical chemistry and reactivity of fluids in confined environment, "host-guest interaction" from transition metal ions (TMI) in zeolites to drug molecules in a microcapsule.

Moreover, quantum chemistry tools together *operando* spectroscopic techniques play an increasingly important role in providing molecular-level description of elementary reaction steps. Therefore, this integrated approach from description of active site architecture to the scale-up of catalytic materials is a key

feature of the laboratory. The performance of the material indeed depends on cooperative properties (site topology, polarity of interfaces, steric constraints, mass transfer, etc.) manifesting themselves on various scales, from the atom to the crystal grain, which are necessary to consider at each step of the catalyst development.

Group 1, Catalysis for Sustainable Development, headed by Dr. Coq, has traditionally focused on problems of green chemistry and environmental catalysis and more recently on new catalysts and processes leading to production of biofuels. Since diesel accounts for ca. 60% of all automotive fuels in France, this research is mainly aimed at production of biodiesel by transesterification of vegetable oils and, to some degree, production of bioethanol from beetroot and corn by biological routes, and conversion of lignocellulosic biomass into syngas with subsequent hydrogen separation and production of liquid fuels (alcohols and alkanes) via Fischer-Tropsch process. The main scientific issues over the *next 10–20 years* are related to the development of renewable resources that will require dramatic improvements in separation technologies. The role of catalysis research in addressing the growing need for inexpensive energy and fuel resources in France is seen in the development of biofuels, which is actively promoted by the government and by the oil industry and agriculture. This research is aimed at second-generation biofuels and complete biomass utilization.

Group 2, Characterization of Advanced Functional Materials. headed by Dr. Di Renzo, is focused on the characterization and application of nanostructured and mesostructured materials. Major research topics include the development of physico-chemical models explaining the formation of porous solids and nanoparticles (zeolites, double-layered hydroxides, micelle-templated materials), the development of their applications in catalytic and adsorption processes (e.g., via surface functionalization and templating of monolithic materials exhibiting hierarchical porosity), and the exploration of new applications of mesostructured materials (e.g., bioinorganic alginate gels and biomolecule-silica composites for controlled drug delivery).

The development of novel materials for healthcare is done in collaboration with *Group 3, Nanostructured Materials for Healthcare,* headed by Dr. Devoisselle, Professor of Pharmaceutical Sciences at Université Montpellier 1 (Medicine). This group focuses on the design of mineral and hybrid nanomaterials, micro- and nano-encapsulation of drugs, physical chemistry of formulation and vectorization, preformulation and formulation of poorly water-soluble drugs, preparation and control of liposomes, as well as evaluation of *in vivo* behavior at the microvasculary scale.

Whereas micelle-templating approaches have been successfully applied in the recent past to obtain novel catalytic materials, the extension of martensitic separation to the nanometer scale may be the next step in the design of new functional materials. These advances have been aided in the past by the development of many *in situ* characterization techniques of the synthesis of nanostructured catalysts, such as various spectroscopic probes and SAXS. The future challenge lies in extending these techniques to characterization of catalyst under working, i.e., *operando*, conditions, in combination with new theoretical tools that can model these phenomena on relevant time and distance scales. The development of a *multiscale modeling toolbox* (so-called deMON) for self-assembled and functional nano-objects is conducted by Dr. Goursot as part of a joint French-Canadian team. The time and distance scales from femtoseconds to minutes and from Å to meters, respectively, are tackled by a combination of quantum mechanical (DFT), semiempirical (DFTB), forcefield (molecular mechanics and dynamics), mesocale and finite element analysis techniques to describe energies, spectroscopic, and reactivity properties; structures, density, and diffusivity; morphology; and mechanical properties of nano-objects.

Group 4, Quantitative and Spectroscopic Approaches to Materials and Their Functions, headed by Dr. Lerner, is currently pursuing the following research directions: studies of adsorption highly hydrophobic molecules in porous solids (e.g. C_{60}, biologically active molecules) and interactions between these molecules and biomolecules; interactions of π-conjugated molecules in excited states (e.g. PAH, polyenes) adsorbed at fluid interfaces (micelles, microemulsions, liposomes) or solid-liquid interfaces (e.g., porous materials); the use of spectroscopic probes to follow adsorption processes in real time, diffusion or reactions at the interfaces, and self-assembly processes (e.g., static and time-resolved fluorescence and IR); optical probes for

biosensors or environmental sensors; photochemistry at interfaces (e.g., isomerization, light-stimulated oxidation).

The development of these various themes in the MACS laboratory is based on the integration of multiple approaches, from the molecular engineering of material precursors to the engineering of the catalytic reaction under scaleable conditions. This integrated approach is made possible by the very composition of the laboratory, consisting of scientists representing different scientific communities, as well as by a close cooperation with other ICGM groups and industrial and academic partners. Fundamental research in MACS is usually supported as part of applied, industrial projects.

SUMMARY AND CONCLUSIONS

The Advanced Materials for Catalysis and Healthcare (MACS) laboratory of the Institute Charles Gerhardt Montpellier is a successful example of a research organization in France where academic and government research is virtually superimposed. CNRS plays a special role in this organization by not only providing research funding (similar to NSF in the United States), but also by providing research staff for joint CNRS-university laboratories. The four research groups of MACS are engaged in cutting-edge research spanning the fundamentals of nanostructured catalyst synthesis, *in situ* characterization, and molecular modeling, as well as the development of new green chemistry technologies aimed at production of fuels from renewable sources, new catalysts and processes for environmental catalysis, and specialty chemical synthesis.

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BACKGROUND

IFP (Institut Français du Pétrole) is an independent research organization founded in 1944 and based in Rueil-Malmaison near Paris, with a second site in Lyon. IFP offers a complete range of services, including upstream, refining, petrochemicals, fuels, and automotive. There are approximately 600 staff members working on downstream research with a budget of approximately €80 million; about 200 staff members work in catalysis research, and about half of the research budget goes to projects related to catalysis. Approximately two-thirds of the funding comes from the French government and one-third from licensing revenues. IFP has about 180 PhD students, of whom ~60 are involved with catalysis projects. IFP functions as the interface between academic groups and industry. Technology that is developed at IFP is licensed to third parties through industrial partners. Spin-off companies resulting from the research results are supported and encouraged by IFP.

As an international research and training center, IFP is developing the transport energies of the 21st century. It provides innovative solutions for a smooth transition to the energies and materials of tomorrow. To fulfill its mission, IFP has 5 complementary strategic objectives:

- Maximize oil and gas exploration and production (upstream sector)
- Maximize conversion oil and gas into energy for transportation
- Diversify fuel sources
- Develop clean, fuel-efficient vehicles (auto sector)
- Capture and store CO_2 to combat greenhouse gases

RESEARCH AND DEVELOPMENT

Approximately 75% of research at IFP is applied, and 25% is basic research. A large amount of research is devoted to traditional downstream refining and petrochemical processes with strengths in residue conversion and distillate hydrotreating (i.e., HDS), hydrocracking of lube oil base stocks, fluid catalytic cracking, aromatic chemical production, environmental (auto-emission catalysts) and biofuels. Basic research at IFP aims to understand the relationship between structure and activity; long-term, the goal is to be able to model

the optimum structure of the catalyst for better performance. (See References section for representative papers from IFP researchers.)

One of IFP's core research areas is the synthesis and development of zeolite and molecular sieve catalysts. In addition to the traditional synthesis methods, a fundamental approach is being investigated for rational synthesis of new catalysts and adsorbants. Substitution of Ge for Si leads to smaller Ge-O-Ge bonds favoring the D4R building blocks. This recognition lead to the synthesis of new material IM-10 (Paillaud et al 2007; Mathieu et al. 2004; Mathieu et al. 2005–U.S. Pat. 6921524B2), illustrated in Figure D.26.

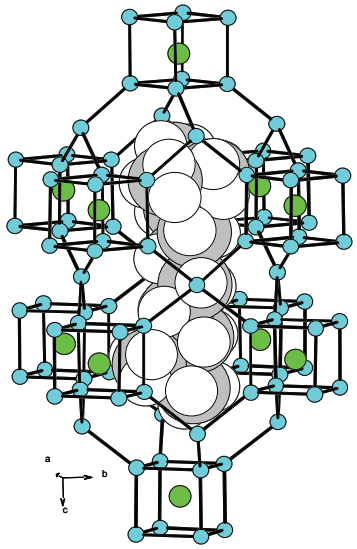

Figure D.26. Structure of new Ge zeolite, IM-10 (courtesy of IFP).

The KFI structure is known for AlPOs but not for zeolites, Figure D.27. Molecular modeling at IFP identified two potential templates required for this structure and subsequently the successful synthesis was developed (Castro et al. 2007; Harbuzaru et al. 2006–U.S. Pat. 7056490B2).

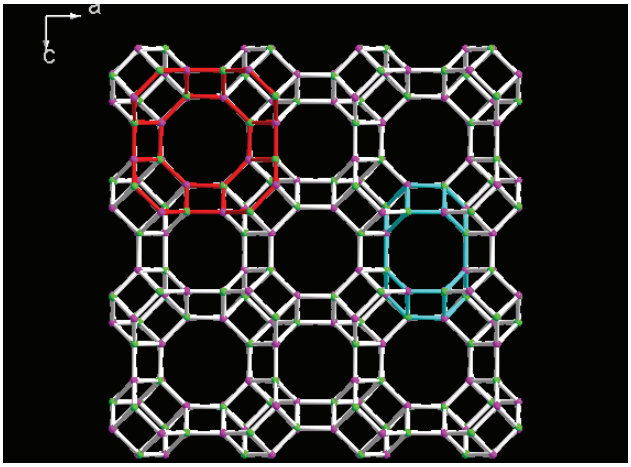

Figure D.27. Molecular model of KFI molecular sieve structure type (courtesy of IFP).

Nanostructured sulfide catalysts are extensively used in refining hydrotreating (HDS) operations for production of clean fuels and are expected to be important catalyst for future biofuels, etc. While these catalysts have been investigated, further improvements are necessary. Effective catalysts promote small MoS_2 particles by Co. A number of synthesis routes have been investigated, leading to higher-activity

catalysts. Traditional synthesis leads to formation of Al-molybdates. Using other mixed Co-Mo oxides leads to smaller particles and better promoter interactions (Cabello, Botto, and Thomas 2000; Martin et al. 2004; Martin et al. 2005). Preparation of Mo-zeolite catalysts with typical Mo compounds leads to external segregation of the Mo. Using cationic Mo-sulfide complexes leads to deposition of the Mo in the zeolite pores.

Supported metal nanoparticles are used in a number of industrial applications. IFP is investigating the effect of particle morphology on the reactivity. Unsupported Pd nano-particles have been prepared with different morphology, Figure D.28. The selectivity for butadiene hydrogenation increases as the fraction of (111) exposed planes increases (Berhault et al. 2007; Bisson et al. 2007).

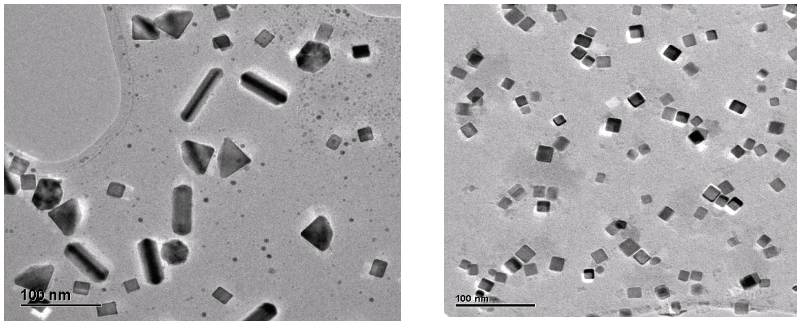

Figure D.28. SEM micrographs of Pd nanoparticles. Left: mix of (110) and (100) exposed crystal planes; Right: cubic morphology with (100) crystal planes (courtesy of IFP).

IFP is one of the first groups using DFT modeling of γ-alumina and anatase-titania to understand the interaction between transition metal sulfide nanoparticles with the support surface. The support can increase the dispersion, alter the structure of the active phase, modify the active sites, or contribute acid-base function to the catalyst. Results of MoS_2 on alumina and titania suggest that the surface interaction leads to a different fraction of exposed S-edge/Mo-edge planes leading to different activity (Costa, Arrouvel, et al. 2007). Pd clusters on alumina interact strongly with Al sites in dehydrated alumina affecting the wetting, nucleation, and diffusion. The adsorption of ethylene on alumina supported Pd_4 clusters depends on the interaction of the cluster with the support, altering the mode of adsorption and leading to differences in the reactivity (Valero, Raybaud, and Sautet 2007).

SUMMARY AND CONCLUSIONS

IFP is a publicly funded technology development company with a wide portfolio of commercial technologies for the energy, petrochemical, and auto industries. In addition, there is a strong emphasis on the fundamentals of science and catalysis. This is supported by a prestigious scientific advisory board, a large number of PhD candidates, and large number of scientific papers published each year. This strong blend of science and technology is focused on delivering new catalysts for today while looking to the future energy needs is unique in the energy industry.

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BACKGROUND

The Institute of Catalysis and Petrochemistry (ICP), the largest research institution in the area of catalysis in Spain, is part of Spain's National Council of Scientific Research (CSIC), an autonomous body belonging to the Spanish Ministry of Education and Science (MEC). The institute is one of the research centers included in the field of Chemistry and Chemical Technologies, which is in turn one of the eight Scientific and Technical Areas of CSIC research, the rest of which are Humanities and Social Sciences, Biology and Biomedicine, Natural Resources, Agricultural Sciences, Materials Sciences and Technology, Food Sciences and Technology, and Physical Sciences and Technology. The Institute consists of 4 Departments: (1) Structure and Reactivity (EAC), (2) Applied Catalysis, (3) Catalytic Process Engineering, and (4) Biocatalysis. The fundamental and applied research in the area of heterogeneous catalysis is conducted in the EAC Department (http://www.icp.csic.es/eac/Index-e.htm), headed by Professor Fierro.

The total 2007 research budget of the EAC Department, excluding staff salaries, is estimated to be ca. €1.5 million (~US$1.73 million at the time of the WTEC visit), which supports a team of 35 scientists consisting of 10 staff scientists, 4 postdocs, 17 PhD students, 4 contracted graduate students, and one administrative staff person. About 55% of this budget comes from competitive projects supported by European Union, national and regional programs, and the other 45% comes from R&D industry contracts. This annual budget increased ~12% over the last 3 years. Approximately half of this funding is provided by the CSIC; the remaining portion comes from research grants from regional and national grant programs, the European Union, and industry sources. In general, the success rate of proposals submitted to national program is rather high, approaching 62% in the areas of energy, materials science, and chemical processes.

Professor Fierro, the ICP vice director, put together a well-organized and compact visit program consisting of introductions, a research presentation on ICP and EAC activities, and a brief tour of laboratory facilities.

RESEARCH AND DEVELOPMENT

The EAC activities are focused on applying sustainable chemistry principles to design new processes and products that minimize the use and generation of toxic compounds and materials. Heterogeneous catalysis plays a major role in this sustainable chemistry research at ICP via (1) the design and production of catalytic nanoparticles, (2) tapping new "greener" feedstocks, (3) novel reactor concepts that cut down pollution and energy consumption, and (4) the development of next-generation catalysts for zero-waste emissions.

Specifically, EAC is pursuing research activities in three critical areas:

1. *Energy*: electrocatalysis and direct methanol/ethanol fuel cell (DMFC/DEFC); hydrogen production by reforming and water splitting under visible light irradiation over band-gap tailored semiconductors (Ins, ZnS, CdS, WS_2, and some novel niobates); and biofuels: biodiesel production on basic solid oxide catalysts (CaO), bioethanol, and its reforming into hydrogen
2. *Environment:* oil refining: sulfur removal and hydrogenation of aromatics, VOC removal, TWC, CO_2 utilization via coal gasification with CO_2, production of acetic acid and hydrogenation into methanol
3. *Clean Catalytic Processes:* selective oxidations: H_2O_2 synthesis, alkene epoxidation; HC autoxidation; FT synthesis: synthetic gasoline, diesel and alkenes; and natural gas conversion: syngas and H_2 production, one-step methanol synthesis

Professor Fierro shared a detailed view on EAC's short-term (5–10 years) and long-term (20 years) research priorities in heterogeneous catalysis by nanostructured materials. The overall vision of future catalysis research is centered on three key issues: (1) development of a hydrogen economy, (2) development of new catalysts that will enable a shift from crude oil to gas- and biomass-based chemistry, and (3) boosting catalytic selectivity to 100% in complex, multistep reactions.

In the short term, EAC's catalysis research priorities should be aimed at (1) achieving superior control in synthesis over structure and properties of nanosized catalytic objects and their assembly into hierarchical structures; (2) integration of catalytic reaction with separation in one reactor in order to break down mass-transfer limitations of current processes; (3) development of nanoscale reactors that may exhibit radically new reactivities due to novel nanoscale confinement effects; and (4) improving methods of understanding working catalysts under dynamic reaction conditions.

In the area of *synthesis of catalytic nanomaterials*, EAC group members are highly interested in the sol-gel preparation of mesoporous phases. Recent successful examples are nanoporous HMS and Ti-HMS phases exhibiting isolated Ti sites and tailored acid properties. Future work will focus on incorporation of other catalytically important metal oxides such as Zr, Cu, Fe, and Mn, as well as on exploring the synthesis of well-defined metal oxide nanoparticles in nonaqueous media. Another promising synthesis approach is deposition of bulk metal nanoparticles as electrode materials for PEM fuel cells employing microemulsion techniques in the presence of nonionic surfactants.

Theoretical methods are gaining great importance in nanocatalysis due to major hardware and software advances; the major challenge in this area is bridging the gap between theory and experiment with respect to temperature, pressure, system size, and time scales. Recent successful examples at EAC of applying theory to problems of catalysis included density functional theory (DFT) calculations of novel homogeneous Mo oxidation catalysts, time-dependent DFT calculations of UV-visible spectra of Ti-containing catalysts as a function of Ti dispersion and interaction with probe molecules, and several others. In these efforts the EAC group is assisted by several computing facilities: CTI in CSIC: (16 Tflop facilities running Gaussian'03, Materials Studio 4.0, etc.), and access to Spain's National Supercomputing network. As a result, the EAC group is acquiring great expertise in the applications of theory to catalysis science.

Nine EAC laboratories occupy 255 m^2 of floor space, industrial projects (bunker reactors) occupy another 34 m^2, and XPS/AES equipment occupies 30 m^2. EAC is well equipped with several *in situ* techniques, such as XRD, Raman, DRIFTS, DEMS, ATR-IR, etc. EAC researchers have access to electron microscopy, MAS-NMR, EELS and XANES/EFAXS at the synchrotron facilities at Grenoble (France), Lawrence Berkeley National Laboratory (CA, USA), and Campinas (Brazil) via collaborations. Among highly desirable but currently unavailable characterization tools at EAC, Dr. Fierro cited (1) CVD and related gas-phase techniques for active phase deposition in non-porous materials, and (2) dynamic SIMS and environmental XPS capable of operating at 1 mbar pressure of reactive gases.

Nanocatalysis is a multidisciplinary effort, and EAC activities in this arena benefit from *international collaborations* with many research groups in Latin America, the European Union, and the United States (e.g., Drs. Salmeron and Iglesia at University of California, Berkeley).

Intellectual property resulting from industry-sponsored projects belongs to the scientists involved in these research projects, whereas industry sponsors receive the right to exploit it. Often these terms are negotiated and agreed by the Technological Transfer Office of CSIC. Individual investigators, laboratories, and institutes receive some financial compensation from patented inventions, but only in those cases where an invention is commercialized. The initial patent filing costs are covered by CSIC, which later makes a determination whether to maintain a patent. When a patent is licensed, all patent costs are recovered by CSIC.

SUMMARY AND CONCLUSIONS

The Institute of Catalysis and Petrochemistry of the Spanish National Council of Scientific Research is a world-class catalysis research institution with significant activities in both fundamental and applied catalysis research. The fundamental and applied research in the area of heterogeneous catalysis is conducted in the Structure and Reactivity (EAC) Department headed by Professor Fierro. EAC is engaged in cutting-edge catalysis research guided by the sustainability principles and aimed at such high-impact areas as energy, the environment, and clean catalytic processes. The physical infrastructure and characterization facilities are outstanding, and the financial support for catalysis research is impressive. EAC successfully blends fundamental approaches, such as theoretical modeling of catalytic processes and *in situ* characterization of catalysts under working conditions, with reaction engineering studies, including semi-pilot-scale testing of real catalysts, to solve current industrial problems. The visiting WTEC team was highly impressed by the detailed and insightful views shared by Professor Fierro and members of his department on future trends and needs in catalysis by nanostructured materials.

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BACKGROUND

The Institute of Research on Catalysis and the Environment of Lyon (IRCELYON) was established on January 1, 2007, by merging two previous institutes: the Institute of Research for Catalysis (IRC) and the Laboratory of Chemistry for the Environment (LACE). The Institute is jointly managed by the Centre National de la Recherche Scientifique (CNRS) and the University of Lyon.

CNRS is a governmental research organization founded in 1939. It is managed by the minister of research in France and had a budget in 2007 of €2.9 billion (~US$4.06 billion[9]). CNRS employs 26,000 people, including 11,000 research scientists and 15,000 engineers, administrators, and support staff. CNRS has 1,200 laboratories throughout France. It has the following missions:

- To evaluate and carry out all research capable of advancing knowledge and bringing social, cultural, and economic benefits for society
- To contribute to the application and promotion of research results
- To develop scientific information
- To support research training
- To participate in the analysis of the national and international scientific climate and its potential for evolution in order to develop national policy

ANR (France's equivalent of the National Science Foundation) has seven governmental priorities:

1. Biology and Health
2. Ecosystems
3. Energy and the Environment (including CO_2 minimization, hydrogen and fuel cells, bioenergy, transport, and clean vehicles)
4. Engineering Processes (including chemistry & processes, materials & processes)
5. Physics and Information
6. Humanities and Society
7. Basic Science (Chemistry & multidisciplinary studies)

[9] Approximate Fall 2007 exchange rate of $1.40.

While catalysis is not one of these top seven priorities, it is a cross-cutting research area that fits into three of the ANR priority categories. These research priorities are set by academia, industry, and government. Institute directors try to lobby politicians to set priorities, however IRCELYON researchers feel that industry has more influence in setting these priorities than academia. The WTEC team's hosts at IRCELYON also said that the research budget in France is going to decrease in the coming years.

The University of Lyon campus known as Université Claude Bernard Lyon 1 with which IRCELYON is affiliated has 30,000 students and 4,500 staff, including 3,252 faculty members. There are 102 research laboratories focused on three areas: (1) Cancer, (2) Environmental Sciences, and (3) Materials, according to university priorities. Each lab is evaluated every 4 years.

Thirty percent of academic research in catalysis in France is located at IRCELYON. There are 7 other laboratories in France that study heterogeneous catalysis. IRCELYON has 7800 m^2 of lab and office space. The lab has 113 permanent researchers whose salary is paid by the government. This includes 46 CNRS researchers, 17 university professors, and 49 technicians and engineers. There are approximately 68 PhD students, 23 post-doctoral researchers, 15 master's students, and 10 undergraduate students working at IRCELYON. Over 30 different countries are represented in the group. Over the last ten years the lab has published over 1371 papers.

The annual budget for IRCELYON is around €11 million (~US$15.4 million) a year. This can be broken down into: €6 million/year for permanent positions (where the funding comes from government, CNRS, and the university), €1 million/year for supplies and equipment (from CRNS and the university), and €4 million/yr from grants and industrial collaborations. The salaries total €1 million/year for post-docs and €2.4 million/year for PhD students.

Because the institute has many industry-sponsored research activities, intellectual property (IP) issues need to be addressed before sponsored research agreements are carried out. These issues are negotiated between IRCELYON and the industry partner after preliminary discussions about the research. IRCELYON requires IP sharing, and patents are generally deposited by the industry partner. Sometimes CNRS may take a patent alone. If the patents are commercialized, direct negotiations are undertaken between CNRS or the university and partner.

The structure of IRCELYON is shown in Figure D.29. The research is divided into 8 research teams. There are 4–5 people on the scientific committee who advise the director on scientific issues. The management style is a bottom-up approach where the research priorities are set by the research team. The group does not currently have theoreticians, but it does collaborate with other theoretical groups at Lyon University. There is generally 1 scientist or technician assigned to each large piece of equipment.

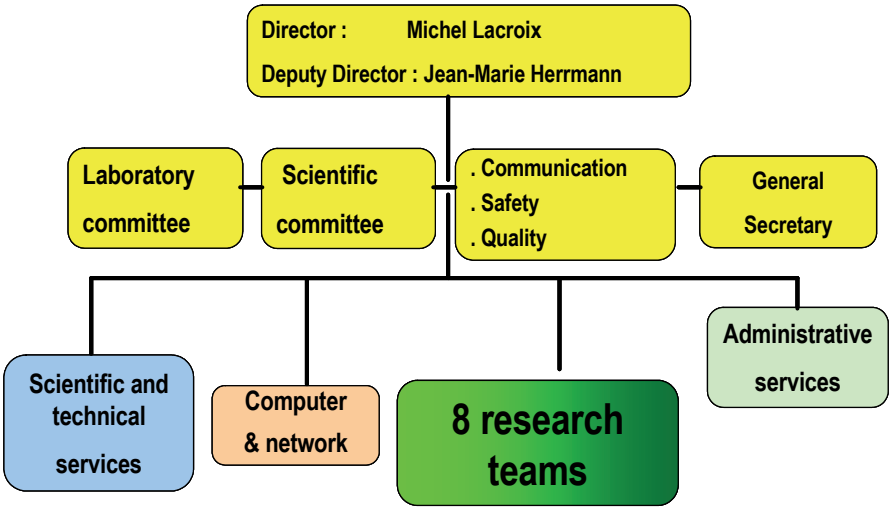

Figure D.29. Organization of IRCELYON.

The WTEC team's hosts at IRCELYON noted that they view the major opportunities in catalysis research in the next 10 to 20 years to be the following:

- By-product and waste minimization
- Air and water treatments
- Renewable feedstocks for biofuels and bioproducts
- Selective oxidation (gas and liquid phase)
- Synthesis of fuels (from natural gas, coal, renewables)
- Improved methodologies (process intensification, high-throughput testing, and supercritical media).

IRCELYON also has many international exchange programs. It has joint laboratories in Russia (Boreskov Institute of Catalysis, Novosibirsk), China (State Key Laboratory of Catalysis, Dalian), and Vietnam. It has research conventions in South America, Japan, and India. It has bilateral programs in Europe with CNRS and the Ministry of Research. It also has contracts with the European Commission, including TOPCOMBI (coordinators), IDECAT, ACENET (coordinators), and STREPs.

RESEARCH AND DEVELOPMENT ACTIVITIES

The goal of IRCELYON is to do fundamental catalysis research on applied problems. The institute is divided into 8 research teams, as outlined below.

1. *Clean and Renewable Energies*

Research in this research team is divided into the following areas:

- Hydrogen production (from methane)
- Hydrogen storage
- Catalytic combustion (natural gas and biogas)
- Fuel cells
- Thermostable catalysts
- Oxidation catalysts
- Calorimetric measurements

The most important areas are hydrogen production, catalytic combustion, and calorimetric measurements.

2. *Engineering and Process Intensification*

This is a large cross-cutting group in IRCELYON that works with many of the other groups. There are 14 staff and 30–40 post-docs in this group. The two major thrusts of this group are (1) high-throughput testing of catalysts and (2) microreactors. Figure D.30 shows a high-throughput reactor that was developed at IRCELYON. The microreactors fit under the process intensification section, which is developing microreactors for producing hydrogen, water-gas shift reaction, and PROX. The microreactors that have been developed for methane steam reforming of hydrogen are significantly more active than larger reactors because of notably improved heat and mass transfer limitations. The group also has a TAP reactor.

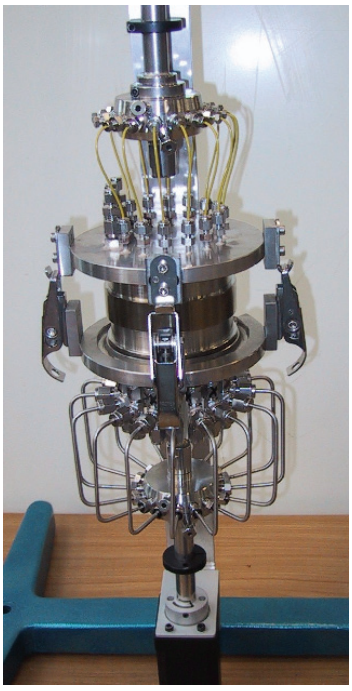

Figure D.30. High-throughput reactor developed at IRCELYON.

The group currently has a large effort on conversion of lignocellulosic material by gasification and pyrolysis routes. The current effort is on upgrading of pyrolysis oils. IRCELYON researchers are studying the

hydrotreating and catalytic cracking of pyrolysis oils mixed with vacuum gas-oil at a 5–10 wt% pyrolysis oil level. The hope is that the pyrolysis oils can be blended with petroleum based feedstocks to meet European mandates on biofuel blending. The group is also performing these studies with model bio-oil compounds.

Other areas of research in this team include intensification of catalytic processes, catalytic membranes, electrocatalytic processes, and advanced kinetics. The catalytic membranes are being used for methane conversion.

See References section for representative publications by this group.

3. *Nanostructured & Functional Materials*

The main focus of this group is on understanding how materials are formed. This group combines molecular chemistry and heterogeneous catalysis. One of the themes is to understand the kinetics of materials synthesis. Some goals of this group include production of high surface area oxides (1) with controlled porosity and specific properties according to application, (2) that can easily be shaped into different forms (pellets, moonlight, membranes), (3) attrition resistance, and (4) high thermal stability. The group is also trying to produce carbon materials with similar properties. Other materials include organic-inorganic hybrid materials.

The areas of study in this group include

- Metal and oxide nanoparticles
- Molecular precursors
- Sol-gel synthesis
- Neutron diffusion
- Nanostructured solids
- Gold catalysts

4. *Refining and Valorization of Hydrocarbons*

The focus of this group is on refining petroleum-based feedstocks. The two major research areas are (1) hydrotreating and (2) conversion of light alkanes. Hydrotreatment methods include HDS, HDM, and HDO, and include study of sulfided properties of metals for deep desulphurization with H_2S or NH_3. The group also studies chalcogenides for hydrotreating reactions. The conversion of light alkanes is primarily by dehydrogenation. This group also contains a number of *in situ* spectroscopy techniques, including Raman, FTIR, and it has access to EXAFS and XANES.

5. *Air Treatment and Atmospheric Chemistry*

This group studies post-combustion problems. There are five areas within this group:

- Micro-Kinetics
- Cold plasma (combined with catalysis)
- $DeNO_x$
- Photocatalysis
- Reactivity and chemistry of dispersed aerosols (specializing in atmospheric chemistry, not catalysis)

6. *Water and Wastewater Treatments*

There are three main research areas in this group:

- Catalytic wet air oxidation
- Photocatalysis
- Adsorption and absorption of pollutants

New processes for the treatment of water and waste water are developed, either to treat traces of pollutants (pharmaceutical compounds, pesticides, HAP, etc.) or microorganisms, or to treat industrial water highly charged in organic wastes refractory to biodegradation The goal with wet air oxidation methods is to use molecular oxygen to convert organic wastes in water (mainly industrial water and sewage sludges) to CO_2. Researchers in this group have several projects on photocatalysis and even have a pilot plant for treating waste water with TiO_2. The photocatalysis effort is aimed at producing drinking water and treating traces of pollutants in waste water. They are also working with biologists to look at the destruction of viruses by photocatalysis.

7. *Surfaces and Interfaces*

The surface and interface group studies model compounds (extended surfaces: poly and single-crystals) and nanoparticles (synthesized by chemical and physical methods). The focus is on surfaces of metals and alloys. The group has a wide range of techniques, including HREELS, FTIR, PM-IRRAS, ISS, XPS, UPS, AES, LEED, TDS, AFM, STM (*in situ* from UHV to elevated pressures), TEM (HRTEM, STEM-HAADF, EDX, PEELS), and SEM (ESEM, HRSEM, Wet-STEM). Group members are studying a range of reactions, including CO oxidation, partial oxidation, and total oxidation, selective hydrogenation of unsaturated hydrocarbons, and NTCs synthesis by hydrocarbon decomposition. They are working to try to bridge the pressure and materials gap between surface science and catalysis. Indeed, an important effort was made to adapt some of the techniques for *in situ* applications at elevated pressures either by developments within the group (STM, PM-IRRAS) or through collaborations at synchrotron facilities (SXRD at ESRF, Genoble; XPS at ALS-LBNL, Berkeley).

See References section for representative publications by this group.

8. *Conversion of Biomass and Green Chemistry*

This is an area that is growing in importance. This group is studying both fuels and chemicals formed from biomass as well as green chemistry processes that use supercritical fluid. Group members are studying trans-esterification of vegetable oils (not edible ones) in supercritical media on solid catalysts. They are also working on enzymatic catalysis where the enzymes are encapsulated in a solid. IRCELYON has done a lot of work on chemical production from biomass, including hydrogenation and oxidation of sugars as well as of glycerol. Recently, IRCELYON started to work on the conversion of cellulose to platform molecules useful as building blocks for chemical synthesis. Other areas of work include using catalysis for fine chemistry with heterogeneous catalysis, organic reactions with the functional catalysis group, and reaction in supercritical media (primarily propane and CO_2).

See References section for representative publications by this group.

SUMMARY AND CONCLUSIONS

In the United States there is no academic- or government-sponsored catalysis research group that compares with IRCELYON in terms of the size of the group, breadth of technology, and funding levels. As environmental and energy issues becoming increasing important to our society, IRCELYON is well positioned for continuing support and further growth. It has the range of expertise in catalysis, engineering, and surface science to make substantial future promising discoveries in the areas of energy and environment.

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Site: **Instituto de Tecnología Química (ITQ)**
Av/ de los Naranjos s/n
46022 Valencia, Spain

Date Visited: September 25, 2007

WTEC Attendee: R. J. Davis (report author)

Host: Prof. Avelino Corma Canós, Scientific Director
Email: acorma@itq.upv.es

BACKGROUND

Instituto de Tecnología Química (ITQ) was founded in 1990 as a joint venture between the Universidad Politécnica de Valencia and the Spanish Council for Scientific Research. Professor Corma started building reactors for the institute while he was in Madrid and moved the research group to Valencia by 1991. At that time, he started to incorporate faculty from the Polytechnic University into the Institute. The grand vision for the ITQ was to bring together expertise in inorganic chemistry for materials preparation, physical chemistry for surface science, and chemical engineering and organic chemistry for reactivity studies, to provide a comprehensive approach to catalysis research. Moreover, the approach taken with institute management allowed for fundamental research to be carried out along with applied research of direct interest to industry.

The institute currently employs 22 researchers; 42 analytical, workshop, lab assistance, and maintenance staff; 6 administrative staff; 28 doctoral students; and 21 postdoctoral researchers, for an overall staffing level close to 100 people. The management structure consists of an administrative director and a scientific director. Professor Corma serves as the scientific director and is in charge of determining the focus of research performed at the institute. In addition to serving as scientific director, Corma also maintains his own research program that is responsible for more than a third of the papers published by institute members. The output of the ITQ in 2006 was 5 PhD degrees, 105 research publications in international journals, and 14 patents, 2 of which were licensed. Collaborations among researchers are strongly encouraged.

Since the university collects 25% nonreturnable overhead from grants and contracts, ITQ has adopted a financial model that reinvests back in the institute all discretionary money derived from industrial contracts. For example, royalties from patents are returned to the institute instead of to the inventors. This model for discretionary funds allowed for a rapid expansion of the institute in terms of equipment and scholarships.

The growth of the ITQ budget throughout the last decade has been remarkable, as illustrated in Figure D.31. By 2006, the income to the ITQ was about €4 million, with over 40% coming from research and development contracts with companies. About 30% of the annual income was derived from competitive grants funded by regional, national, and European Union agencies, and about 17% was obtained from licensing fees generated by patents developed at the ITQ. Many major international chemical and energy companies work regularly with the institute. Although graduate student tuition is very low at the ITQ, it is paid directly by the student. Government scholarships fund the research stipend for about half of the students at the ITQ, and a combination of research contracts with discretionary funds supports the others.

RESEARCH AND DEVELOPMENT

The research programs at the ITQ involve various aspects of catalyst synthesis, materials characterization, and catalytic applications. Professor Corma is well recognized for his work on zeolite synthesis and catalysis. Efforts in materials synthesis have also included acid/base solids as well as supported metals. Quantum chemistry and molecular simulation is used to provide important insights into each aspect of the research program. For example, theory is used to predict the stability of zeolite frameworks containing heteroatoms prior to attempting a synthesis method. Currently, three people in the ITQ are involved with theory and simulation.

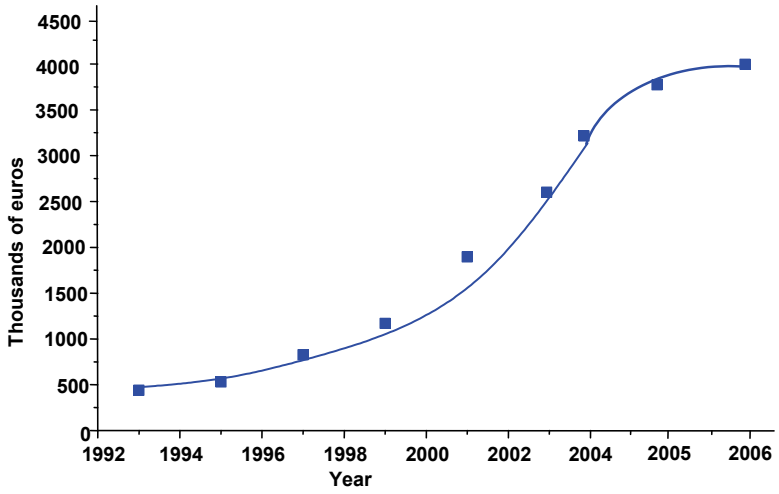

Figure D.31. Annual income at the ITQ (courtesy of A. Corma).

The applications area at ITQ is focused mainly on refining, petrochemistry, and fine chemicals, utilizing primarily molecular sieves and amorphous solid acid catalysts. For oil refining, reactions such as catalytic cracking, isobutene/butene alkylation, olefin and paraffin isomerization, hydrodesulfurization, hydrodenitrogenation, and Fischer-Tropsch synthesis are actively pursued. Reactions of interest in the petrochemistry area are aromatic alkylation, alkylaromatic isomerization, and selective oxidation of alkanes. In the fine chemicals arena, the ITQ is exploring esterification, alkylation, acylation, acetal formation, C-C bond formation via Heck and Suzuki coupling, gold catalysis, selective oxidation, and catalytic reactions in ionic liquids or polyethyleneglycol solvents. Such a broad spectrum of reactions being studied within a single institution is quite unusual. Moreover, the institute has a pilot-plant-scale operation on site to allow for direct testing of industrially relevant catalysts.

The researchers at ITQ have developed and make extensive use of high-throughput methods and tools to synthesize and test new catalysts. For example, Figure D.32 shows one of the robots developed for the synthesis of zeolite materials. The left part of Figure D.33 presents a parallel reactor assembly used for fixed bed that was developed at ITQ and is now commercialized by Amtec; the right part shows an automated assembly of batch reactors.

Figure D.32. Robot used for automated synthesis of zeolites (courtesy of A. Corma).

Figure D.33. High-throughput reactors at the ITQ. The left photo shows a parallel flow reactor; the right photo shows an automatic batch autoclave system (courtesy of A. Corma).

The institute is equipped with a wide array of catalyst characterization instruments for analysis such as physical adsorption, temperature-programmed desorption, X-ray diffraction, thermoanalysis, calorimetry, and spectrometry (FT-IR, UV-Vis, Raman, NMR, Auger, and XPS) and has ready access to analytical electron microscopy (TEM and SEM).

Although researchers at the ITQ perform fundamental characterization and modeling studies of synthetic catalysts, the high-throughput synthesis and testing facilities allow for a combinatorial approach to catalyst optimization. For example, over 200 alkylation catalysts and over 100 de-alkylation/transalkylation catalysts were prepared and tested in the high-throughput facilities of the ITQ. In the latter case, a new optimized material that rivals the performance of industrial catalysts has reached pilot plant stage. Additional combinatorial studies involve sulfur and water-resistant acid catalysts for isomerization of alkanes as well as promoted mixed metal oxides (Mo, Te, V, Nb) for selective oxidation of alkanes. With the ability to obtain large data sets at the ITQ, researchers are now employing artificial neural networks to create models capable of predicting reactor performance. Extensive experimental results are used to "train" an artificial neural network to successfully predict behavior of a reactor accomplishing oxidative dehydrogenation of ethane.

A new direction at the ITQ involves combining the acid/base functionality of a support with an active organometallic component to create new catalysts. In addition, ITQ scientists are exploring the concept of cooperativity in acid/base catalysis by appropriately spacing the acid and base sites on solid surfaces. Research at the ITQ also involves new materials with applications beyond catalysis. For example, materials with defined size and shape are being explored as photonic crystals and for use in photovoltaic cells. Other materials with defined porosity and composition are useful in drug delivery, as light-emitting devices, or for controlling release of semiotic compounds. Finally, multifunctional materials used as sensors, photoluminescent devices, and magnetic devices are also being explored.

SUMMARY AND CONCLUSIONS

The ITQ is a relatively new institute that has experienced extremely rapid growth under the scientific leadership of its director, Professor Avelino Corma. It is now widely regarded as one of the top producers of catalysis knowledge in the world, and Corma continues to be recognized as a leader in the field. The institute was in the process of expanding its facilities during the WTEC visit, and all signs point to continued success. The institute maintains a significant number of industrial contracts (almost half of the budget) while still maintaining a fundamental approach to catalysis. The portfolio of activities appears to be a good combination of both basic and applied research in catalysis, which is not typical of U.S. laboratories.

Site: **Max-Plank-Institut für Kohlenforschung**
1 Kaiser Wilhelm Platz
45470 Mülheim an der Ruhr, Germany
http://www.mpi-muelheim.mpg.de/kofo/english/mpikofo_home_e.html

Date Visited: September 25, 2007

WTEC Attendees: J. Miller (report author), L. Thompson, M. Neurock, J. Regalbuto, M. DeHaemer

Host: Prof. Manfred T. Reetz, Director
Dept. of Synthetic Organic Chemistry
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Email: reetz@mpi-muelheim.mpg.de

BACKGROUND

The Max-Plank-Institut für Kohlenforschung (Max Planck Institute for Coal Research) was founded in 1912 by the Kaiser Wilhelm Society, the coal industry, and the town of Mülheim/Ruhr. The first director was Franz Fischer, who conducted basic research on the chemistry of coal, which lead to the Fischer-Tropsch process. In 1943, Karl Ziegler was appointed director and the main emphasis in the institute shifted to organometallic chemistry. In 1993, Manfred Reetz became director and redefined the research activities, establishing the five departments that exist today (see Research and Development section below). Currently, the institute has 205 staff members, of whom 50 are scientists. In addition, there are more than 100 graduate, post-graduate, and visiting scientists working at the institute. The institute comprises five departments, each headed by a director: Department of Synthetic Organic Chemistry (Director: M. T. Reetz), Department of Homogeneous Catalysis (Director: B. List), Department of Heterogeneous Catalysis (Director: F. Schüth), Department of Organometallic Chemistry (Director: A. Fürstner), and Department of Theory (Director: W. Thiel). The position of Managing Director rotates every three years.

The departments are supported by a variety of analytical service groups, which also carry out independent research. These groups include NMR Spectroscopy (Dr. Mynott; http://www.mpi-muelheim.mpg.de/kofo/institut/forschungsinfrastruktur/nmr/mynott_e.html), Electron Microscopy (Dr. Tesche; http://www.mpi-muelheim.mpg.de/kofo/institut/forschungsinfrastruktur/tesche/tesche_e.html), X-ray Structural Analysis (Dr. Lehmann; http://www.mpi-muelheim.mpg.de/kofo/institut/forschungsinfrastruktur/kristallographie/lehmann_e.html), Mass Spectroscopy (Dr. Schrader; http://www.mpi-muelheim.mpg.de/kofo/institut/forschungsinfrastruktur/ms_schrader/ms_group.html), and Chromatography (Dr. Belder; http://www.mpi-muelheim.mpg.de/kofo/institut/forschungsinfrastruktur/chromatography/belder_engl.html). In addition, there is a central Computer Group (Dr. Koslowski; http://www.mpi-muelheim.mpg.de/kofo/institut/forschungsinfrastruktur/computer/mpikofo_comp.html), which is also involved in software development (e.g., MassLib; http://www.masslib.com/).

Catalysis is viewed as the key technology in the establishment of economically and ecologically sound chemical processes of the future. The departments take an interdisciplinary approach to development of new catalysts and reactions. The primary research focus of the institute is on reactions rather than materials. The goals of the institute are to develop new methods for selective and benign synthesis of compounds and materials. This is achieved by increasing activity, selectivity, minimization of energy, minimization of the number of reaction steps, increased atom efficiency, and development of green chemistry processes.

RESEARCH AND DEVELOPMENT

Department of Synthetic Organic Chemistry (M. T. Reetz, Director)

- New catalytic systems in organic chemistry
- Research in polymer chemistry
- Coal transformations

- Catalysis in supercritical CO_2
- New methods for enantioselective catalysts
- Enzyme catalysis, especially directed evolution as a means to create enantioselective biocatalysts

Department of Homogeneous Catalysis (B. List, Director)

- Reactions of organometallic catalysts
- Enantioselective reactions by organocatalysts (nonmetallic)
- Synthesis of chiral compounds

Department of Heterogeneous Catalysis (F. Schüth, Director)

- Controlled synthesis of catalytic solids, especially by novel methods
- High-throughput methods for new material synthesis
- Catalytic H_2 storage materials
- Porous and high-surface-area materials, especially mesoporous materials (oxides, phosphates, and nitrides); nanocasting of mesoporous silica and carbon
- Fuel cell catalysts
- Optical materials

Department of Organometallic Chemistry (A. Fürstner, Director)

- Alkene and alkyne metathesis
- Cross-coupling reactions by Fe rather than Pd
- Novel heterocyclic carbene and carbene complexes
- Pt-catalyzed skeletal rearrangements
- E-selective semireductions of alkynes
- Asymmetric hydrogenation of heterocycles
- Total synthesis of bioactive natural products

Department of Theory (W. Thiel, Director)

- Improved computational methods for complex systems: semiempirical, quantum mechanical/molecular mechanical (QM/MM), and multiscale approaches
- Accurate *ab initio* vibration-rotation spectroscopy predictions for small molecules
- DFT modeling of Zieglar-Natta polymerization enantiomeric hydrogenation, Ru catalyzed olefin metathesis, stereochemistry of zirconocene catalyzed olefin polymerization, Pd catalyzed cross-coupling
- Biocatalysis: mechanism of enzymatic reactions

Highlights

A few selected highlights are as follows. A process of directed evolution of enzymes for identification of stereoselective reactivity with formation of thousands of mutant enzymes leads to enzyme catalysts with high enantioselectivity. The schematic process is shown in Figure D.34. Enzymes such as lipases, epoxidases, and oxidasese have been studied (Reetz Group: Reetz 2002a; 2002b; 2002c; Reetz and Rüggeberg 2002). This approach has lead to some exceptionally high selectivities compared to original enzyme or use of organometallic catalysts.

Most homogeneous catalysts contain transition metal atoms; however, metal-free enantio-selective homogeneous catalysts have been developed for numerous reaction types, as shown in Figure D.35 (List Group: Hechavarria Fonseca and List 2004).

The first metal-free catalytic asymmetric hydrogenation catalyst for reduction of α,β-unsaturated aldehydes via dihydropyridine gives high yields, is chemo- and entio-selective and has applications to synthesis of chiral pharmaceuticals (List Group: Yang, Hechavarria Fonseca, and List 2004).

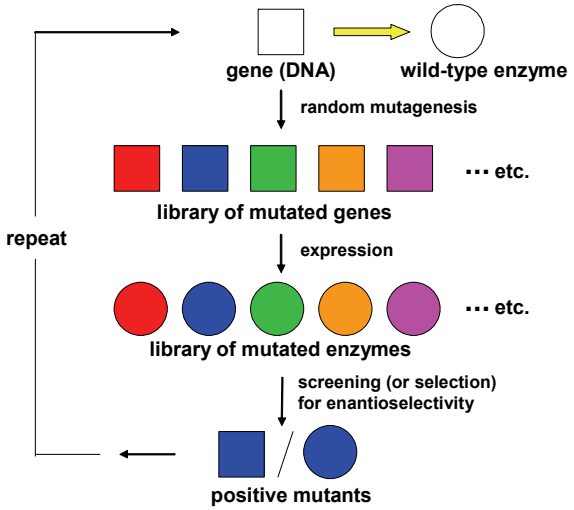

Figure D.34. Schematic process of high-throughput screening to identify enantioselective enzymes followed by growth of higher selective mutant enzymes.

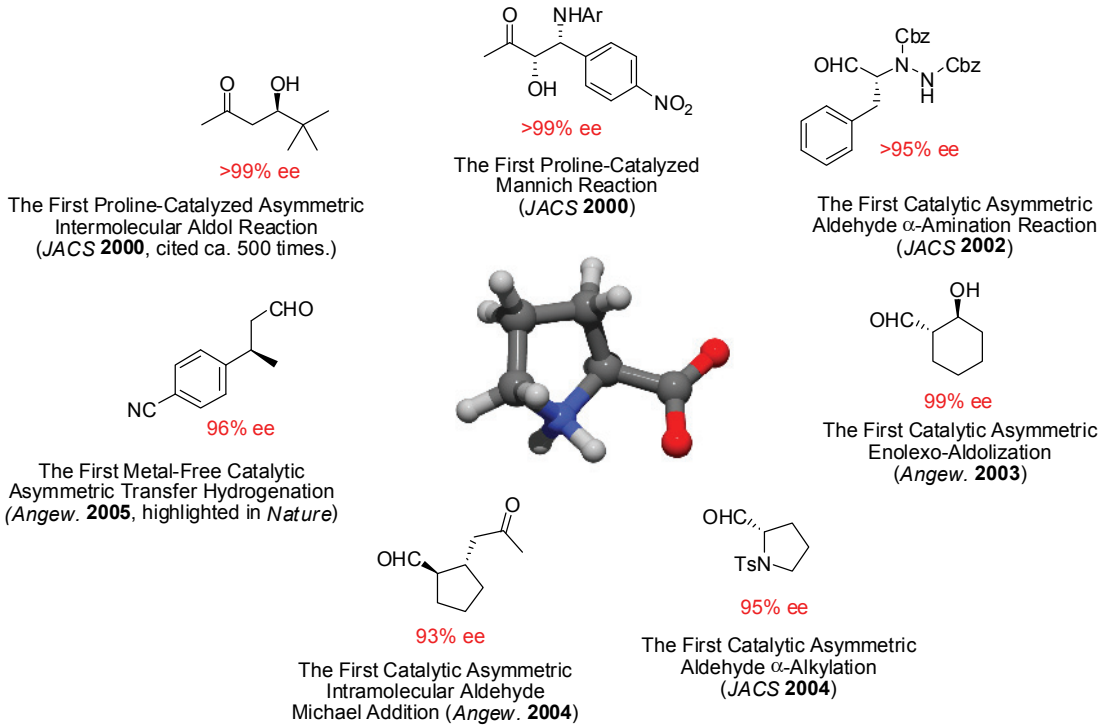

Figure D.35. Metal-free, enatioselective organo-catalyst and reactions.

New selective catalysts for synthetic organic transformations using such transition metals as Fe, Pt, Au and Ru in combination with novel ligands have been developed (Fürstner Group). Applications based on novel strategies in natural products synthesis have lead to a drastic reduction in the number of steps, allowing for atom economy and green chemistry (Fürstner Group).

The application of theory using QM as well as MM in polymerization, transition metal catalyzed selective transformations and enzyme-catalyzed enantioselective processes have helped crucially in the development of new catalyst systems (Thiel Group).

The synthesis of mesoporous carbons as a support for supported metals involves the synthesis of ordered mesoporous oxides like SBA-15. Ferromagnetic $CoFe_2O_4$ can be nano-cast into the structure. Mesoporous carbons are prepared by incorporating carbon precursors and curing at high temperature. Dissolution of the silica leaves a high-surface-area, mesoporous carbon support with magnetic particles, Figure D.36 (Schüth Group: Schwickardi et al. 2002; Lu et al. 2003; Lu, Keifer, et al. 2004). These supports can be used to deposit catalyst metals and may be easily separated with a magnetic field (Schüth Group: Lu, Li, et al. 2004).

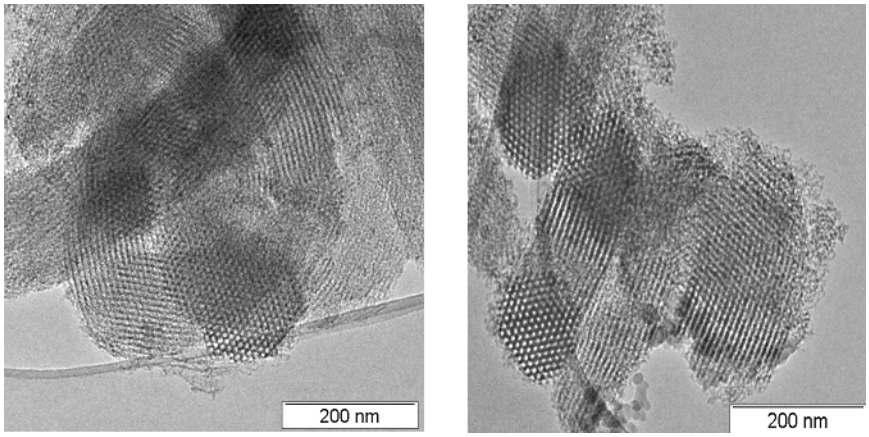

Figure D.36. Electron micrographs of (*left*) mesoporous silica and (*right*) mesoporous carbon.

SUMMARY AND CONCLUSIONS

Max-Plank-Institut für Kohlenforschung (Max Planck Institute for Coal Research) is one of the leading chemistry institutions in Germany. The research programs are supported by a large number of highly skilled, permanent support staff to supply reaction engineering and analytical needs. In addition to the scientific mission, the institute trains a large number of doctoral and postdoctoral students. Finally, the institute has a long history of transferring basic research in chemistry to industrial applications and participating in jointly funded industrial research. The licensing department files patents, licenses technology to industrial partners, and enforces intellectual property rights. The IP department also assists researchers who want to form startup companies based on results and know-how from the institute.

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Sites: **Politecnico di Milano and Università degli Studi di Milano**
Milan, Italy

Date Visited: September 24, 2007

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BACKGROUND

During a full-day workshop at the University of Turin, the WTEC visiting team met with representatives from several Italian institutions involved in catalysis research and development. This site report covers discussions the team had with representatives from institutions in Milan.

There are two catalysis research programs in Milan, Italy. The first, the Laboratory of Catalysis and Catalytic Processes (LCCP; http://www.nemas.polimi.it/research.php?id_group=3) is part of the Center for Nano-Engineered Materials and Surfaces (NEMAS; http://www.nemas.polimi.it/), which is located at the Politecnico di Milano (http://www.polimi.it/english/). The WTEC team met with laboratory head and group leader Professor Pio Forzatti. NEMAS is an interdisciplinary research center established in 2003; this center is accredited by the Italian Ministry of Research as a center of excellence. It supports 50 academics and technicians and 40 post-doctoral scholars and PhD students from the Departments of Chemistry, Physics, Electronics, and Nuclear Engineering ("Giulio Natta"). Most of the center's work can be classified as applied research and is funded nearly equally by the government and companies. The catalysis work involves 10 faculty members, 3 post-doctoral scholars, 3 technicians, 6 PhD students, and approximately 20 students involved in Master's thesis work.

The second program is the Chemical Kinetics, Catalysis, and Applied Physical Chemistry section of the Università degli Studi di Milano (University of Milan) Department of Physical Chemistry and Electrochemistry (http://www.dcfe.unimi.it/presentazione-english.htm). The WTEC team met with Professor Lucio Forni of the section. Prof. Forni's research group is active in heterogeneous catalysis, especially gas-solid reactions for industrial applications.

RESEARCH AND DEVELOPMENT

Politecnico di Milano, NEMAS, Laboratory of Catalysis and Catalytic Processes

Catalysis research at NEMAS focuses on nanostructured coatings for environmental catalysis and nanostructured functional surfaces of carbon, metals, and transition metal oxides. Much of the work is accomplished using commercial catalysts and involves the development of models. Current projects include

- Development of kinetic and mechanistic models for commercial V_2O_5-WO_3/TiO_2 and zeolite-based NH_3 selective catalytic reduction (SCR)

- Preparation and characterization of highly dispersed Pt-Ba and Pt-K catalysts for use in NO_x and soot removal from stationary and mobile sources
- Development of supported Rh catalysts for the short contact time catalytic partial oxidation of natural gas, liquified petroleum gas, and biofuels
- Development of novel Pd-based catalysts for the combustion of CH_4
- Modelling of Fischer-Tropsch synthesis and selective oxidation catalysts
- Use of monolithic reactors for non-isothermal and non-adiabatic processes
- Forming and coating of structured ceramic supports
- Microkinetic modeling of heterogeneous reactions

University of Milan

Catalysis research programs at the University of Milan focus on the preparation of catalysts using flame pyrolysis (FP) methods (see Figure D.37), deposition of catalytic species on honeycomb supports, and development of materials for the photocatalytic dissociation of water. Highly crystalline, phase pure perovskites with surface areas up to 120 m^2/g have been produced using the FP method.

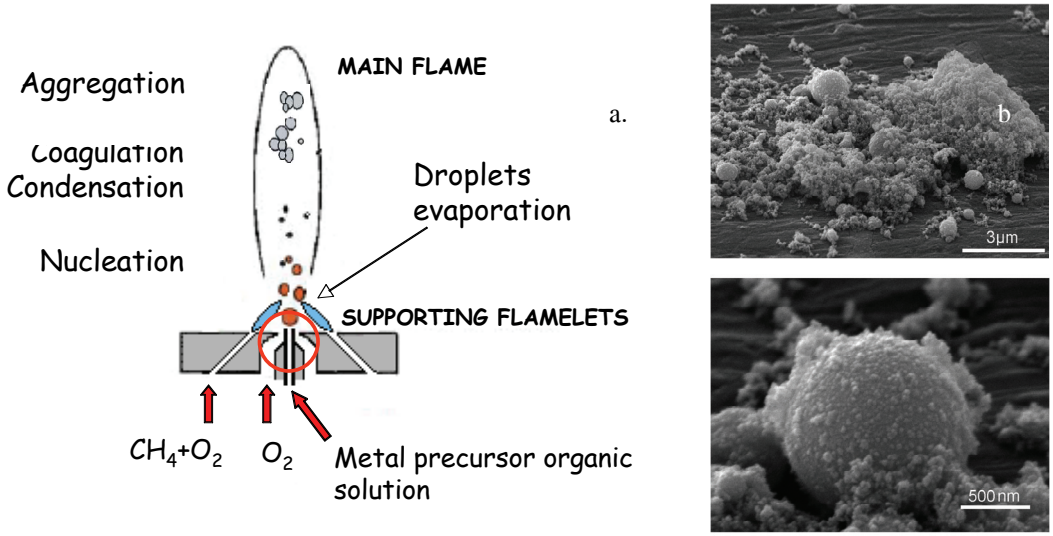

Figure D.37. Schematic of the flame pyrolysis method (a) and scanning electron micrographs of the $LaCoO_3$ product with surface area of 76 m^2/g.

The FP method is also being used to produce TiO_2 for the photocatalytic dissociation of water. This method yields material with a higher hydrogen production rate than Degussa P25. The deposition of Au onto surfaces of the TiO_2 resulted in a significant increase in rate (see Table D.1). It is not clear if the enhanced rate is due to an increase in the photocatalytic activity or a reduction in the band gap. Similar materials are also being developed for the photocatalytic reforming of organic waste to produce hydrogen.

Table D.1. Photocatalytic activity of TiO_2 and Au/TiO_2 at University of Milan

	In H_2O		In H_2O + 6 vol% CH_3OH	
Photocatalyst	H_2 production rate (µmol H_2 h^{-1})	Relative rate	H_2 production rate (µmol H_2 h^{-1})	Relative rate
TiO_2 (P25)	2.46	1.0	170	1.0
FP-TiO_2	3.75	1.5	292	1.7
THPC 1% Au/TiO_2	30.3	12.3	-	-
FP-1% Au/TiO_2	52.4	21.3	7894	47

SUMMARY AND CONCLUSIONS

Research at Politecnico di Milano and Università degli Studi di Milano in the area of catalysis by nanostructured materials is primarily focused on developing a better understanding of currently available catalytic materials. New materials are also being developed for SCR, partial oxidation, and photocatalytic processes. Of particular interest is the work on FP-derived materials for use in the photocatalytic dissociation of H_2O.

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Date Visited: September 26, 2007

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BACKGROUND

Shell has more than 100,000 employees and is active in approximately 130 countries worldwide. It produces about 3.5 million barrels of oil equivalent per day and spends nearly $900 million per year on R&D. The Shell research laboratories were established in Amsterdam in 1914. A second research center is located in Houston, TX, and others have been built in Europe. A new site in Bangalore, India, was under construction at the time of the WTEC team's visit. In 2005, Shell's research and technology center in Amsterdam was taken over by Shell Global Solutions. A new technology center in Amsterdam is currently under construction; when completed in 2008, it will provide over 80,000 m^2 of laboratory and office space. With a focus on finding and delivering oil and gas for world energy needs, Shell is also looking at alternative energy resources, including renewable energy, such as wind, solar, biofuels, hydrogen, and GTL. In addition, reduction of CO_2 remains an activity across all business sectors.

RESEARCH AND DEVELOPMENT

Shell conducts research on oil and gas production (upstream), and refining and chemical processes (downstream), which can also be licensed to third parties. The emphasis in downstream research is to improve refining margins, increase capacity with existing units, and improve safety and the environment to gain a competitive edge. In addition, Shell is looking at tomorrow's potential problems, including trying to reduce CO_2 emissions, increase energy efficiency in processes, integrate the supply chain, develop cleaner processes and fuels, and clean up the environment. All projects are done with multidisciplinary teams of scientists with expertise in chemistry/catalysis, chemical engineering, analytical characterization, design and economic evaluations, business and strategy, and intellectual property. These programs are aligned with business needs.

While current energy demands are met primarily by oil and gas, it is expected that beyond 2025 energy sources will diversify to include biomass, H_2 for fuel cells, wind, solar, etc. (as shown in Figure 8.1). While first-generation biofuels will come from starch, sugars, and vegetable oils, it is expected that longer-term, conversion of lignocellulose will become an important source of energy. However, the demand for oil, gas, and coal is also expected to remain strong in coming years. Finally, the importance of CO_2 management is expected to increase, and Shell is developing sequestering technology and other approaches to this problem.

Some of the scientific challenges recognized at the Shell research and technology center are

- Ultralow-sulfur fuels
- Upgrading heavy oils (including biocrude)

- Syngas to fuels and chemicals
- Selective oxidation of hydrocarbons to oxygenates
- Heterogeneous catalysts in H_2O

On precompetitive research, Shell is also an industrial partner with university programs on fermentation of cellulosic sugar, development of new catalytic materials, new products, and new analytical methods. In addition to the scientific results, Shell scientists have access to experts and their colleagues.

Fundamental research conducted by Shell looks to understand the relationship between structure and performance. New *in situ* catalyst characterizations are developed in collaboration with Utrecht University.

SUMMARY AND CONCLUSIONS

The Amsterdam Research & Technology Centre of Shell Global Solutions is a large industrial laboratory for development of sustainable energy and clean fuels from crude oil and natural gas. Its strengths are in low-sulfur fuel, heavy crude processing, and syngas technologies. Current research is on developing more efficient processes and catalysts to provide a competitive advantage, comply with regulatory guidelines, and to reduce CO_2 emissions. Longer-range, precompetitive research is done through joint ventures with other industry partners and universities and the company participates in several partnerships connected with biofuels production. New materials and analytical characterizations are conducted through university research. Shell has a long history of new technology development in the downstream refining and chemical industries and licenses these to third parties.

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Further information on the “future energy challenge” and emerging “technology challenges” are available on Shell’s website, http://www.shell.com.

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BACKGROUND

The Technische Universität München (TUM) was founded as a "polytechnic school" in 1868 and from the very beginning played an active role in transforming Bavaria from an agricultural state to a high-tech location. Rooted in this tradition, TUM has been transformed over the years into an international university, where one in every four undergraduates within a total student body of approximately 21,000 comes from abroad. Moreover, TUM launched an outpost in Singapore, which goes by the name of the German Institute of Science and Technology (GIST). The range of subjects offered at TUM is unique in Europe: natural sciences, engineering, medicine, and life sciences. Apart from twelve faculties, there are central institutes and research platforms where interdisciplinary competencies for future-oriented research projects are pooled. TUM participates in European university networks, has double diploma agreements with more than 20 universities, and maintains partnerships with more than 130 universities throughout the world.

The Department of Chemistry at TUM is one of the top chemistry departments in the world. Four faculty members of this department were recipients of the Nobel Prize: Robert Huber in 1988 (with Johann Deisenhofer and Hartmut Michel) for "the determination of the three-dimensional structure of a photosynthetic reaction center"; Ernst Otto Fischer in 1973 (with Geoffrey Wilkinson) for "their pioneering work, performed independently, on the chemistry of the organometallic, so called sandwich compounds"; Hans Fischer (1930) for "his researches into the constitution of haemin and chlorophyll and especially for his synthesis of haemin"; and Heinrich Wieland (1927) for "his investigations of the constitution of the bile acids and related substances." The Chemistry Department is home to 16 full and 8 associate professors, 120 academic researchers (financed by the university), 215 academic researchers (financed by third-party funds), 125 technical and administrative staff, 480 graduate students, and 900 undergraduate students. It should be noted that graduate students do not get university support during first 1.5 years while studying toward an intermediate MS degree. They are supported during the last 3 years when they are actively engaged in PhD research. Currently, about 30% of graduate students are international. However, their numbers are growing, and it is expected that in several years up to 70% of all chemistry graduate students will be international.

TUM is the only European university in which a complete spectrum of skills from fundamental science to process engineering is successfully practiced. In particular, a unique portfolio of skills is assembled at TUM

in a catalysis consortium, the Bavarian Innovation Center for Catalysis (BayCat) chaired by Professor Lercher and ranging from molecular and heterogeneous catalysis to preparation of solid materials, from polymerization catalysis to biocatalysis, and from surface science theory to applied electrocatalysis. BayCat members are 14 TUM professors and their research groups in the Departments of Chemistry, Physics, and Mechanical Engineering.

RESEARCH AND DEVELOPMENT

The current research of BayCat is focused on five major research themes:

1. Selective activation of chemical bonds (bifunctional catalysis, catalysis through tandem reactions)
2. Manipulation of C-C, C-O, C-N, C-S, and C-Cl bonds (chemo- and stereoselective catalysis)
3. Transport, sorption, and complex formation (agostic interactions in complexes; directing reactivity through interactions)
4. *In situ* and *operando* characterization (molecular spectroscopy: IR, Raman, NMR; electronic information: XAS, INS, ESR; proximal probes: AFM, STM)
5. Design and synthesis of catalytic materials (size-selective metal catalysis; nanoporous materials), aimed at broadening the basis for raw materials to include gas, crude oil, coal and bioresources

Future developments of BayCat include construction of a new Catalysis Research Center in 2009-2012, which will bring all members under one roof and further bolster research collaborations. This center will have 8000 m^2 of well-equipped laboratory space, 1500 m^2 of offices and seminar rooms, 400 m^2 of high-pressure facilities, and 330 m^2 of pilot plant facilities. Moreover, at least four new hires are planned in near future: in theoretical chemistry to fill the position occupied by Notker Rösch after his planned retirement in 2008; in colloid chemistry, electrochemistry, and molecular biocatalysis.

The funding in the Chemistry Department (ca. €9 million/year) comes from three equally important sources: closed (i.e., noncompetitive) government funding (one-third of the total), open (i.e., competitive) government funding (one-third of the total), and industrial contracts (one-third of the total). The BayCat consortium brings in about 40% of that annual amount. It should be noted that the success rate of research proposals is 20–25% for proposals submitted to the Research Foundation of Germany (DFG) versus about 5% for European Union proposals. A major recent donation of funds and research equipment by Wacker Chemical enabled the department to fund 40 additional PhD students in polymer research and strengthen its focus in this area.

The BayCat members present at the meeting with the WTEC visiting team provided an overview of the current research, falling into six broad themes:

1. *Molecular catalysis – Research topics I and II*: This research is concerned with solvent-stabilized transition metal cations as polymerization catalysts (e.g., Kühn et al. 2007) and ethylene epoxidation catalysis employing Mo complexes (e.g., Kühn et al. 2006).
2. *Inorganic chemistry – Research topics I and II*: Oxidation chemistry with Re complexes, the use of N-heterocyclic carbenes as ligands for catalysis, organocatalysis, and transition metal catalysis (e.g., Herrmann et al. 2007; Baskakov et al. 2007).
3. *Chemical and environmental catalysis* (Prof. Lercher): Solid acid alkylation, catalysts for deep hydrotreating, amine synthesis, transport phenomena in catalysis.
4. *Surface coordination chemistry – Design of well-defined metal centers on solid surfaces* (Prof. Köhler): Synthesis of Pd nanoparticles on surfaces (alumina, carbon) for fine chemical synthesis by solid catalysts via C-C coupling reactions in liquid phase; NO SCR by hydrocarbons and selective oxidation; surface modification of oxide nanoparticles to achieve a controlled distribution in two-phase solvent systems (multiphase catalysis).

5. *Exploration of size-selective properties of metal nanoparticles* (Prof. Heiz):

   I. Cluster catalysis and chemical sensors: guiding principles for understanding cluster catalysis employing TPD, p-MBRS, FTIR, MIES, UPS, microcalorimetry

   II. Optical properties and photocatalysis: mechanisms of photochemical processes in non-scalable size regime employing PDS, p-MBPRS, FTIR, TOF, TOF-PES, CRDS

   III. Electrocatalysis: quantum size effects in electrocatalysis (Dr. A. Arenz, group leader) employing DEMS, FTIR, RDE, clusters suspended in electrolyte)

   IV. Local probes (STM/AFM). The major goals of this research are (a) the exploration of the size-dependent properties of the elements in the Periodic Table; and (b) tuning of physical and chemical properties by changing size, morphology, and chemical composition of nanoparticles. This research is focused on preparation of nanomaterials consisting of monodisperse metal clusters consisting of up to 100 atoms and investigation of their chemical, catalytic, photocatalytic, electrochemical, and optical properties. One of the major results of this research was an impressive demonstration that small gold clusters containing exactly 8 Au atoms are uniquely active in CO oxidation, whereas both smaller and larger Au clusters were essentially inactive in this reaction.

6. *Particle technology and multiscale modeling*: This research is focused on understanding the various steps in catalyst synthesis in order to design improved particulate catalysts for future processes and new reactor configurations. Multiscale modeling will play a major role in this effort by describing the various processes occurring during catalyst synthesis or catalytic reaction on different distance scales, from microscopic scale (quantum mechanics) and mesoscopic scale (statistical thermodynamics) to macroscopic scale (continuum engineering modeling).

SUMMARY AND CONCLUSIONS

BayCat is a consortium of university researchers from the Chemistry, Physics, and Mechanical Engineering Departments at the Technical University of Munich. The vibrant BayCat community is actively engaged in many facets of catalysis research, such as molecular (including polymerization catalysis), heterogeneous catalysis (chemical and environmental), catalysis by nanostructured materials, size-dependent phenomena in metal catalysis, catalysis theory, particle technology, and multiscale modeling, to name a few. BayCat successfully combines fundamental research in nanostructured catalytic materials with more applied pursuits of catalyst synthesis, physico-chemical characterization (including *in situ* and *operando* methods) and pilot-scale testing of industrial catalysts. BayCat appears to be in a growth mode, with plans to begin construction of a new Catalysis Research Center in 2009 and to hire several new faculty members in key growth areas.

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TUM Department of Chemistry, homepage (English). N.d. http://www.ch.tum.de/base/index_e.htm.

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BACKGROUND

The Department of Chemistry at Cambridge has very strong effort in surface science and catalysis. There are formally four professors and three research faculty members who work in the general areas of surfaces, interfaces, and heterogeneous catalysis. This group includes Drs. A. Alavi, S. M. Clarke, P. B. Davies, S. Jenkins, and Professors B. F. G. Johnson, W. Jones, D. King, and R. M. Lambert. Professor Sir David King and Professor Richard Lambert are two of the world's leading experts in the development of novel methods and their application to elucidating fundamental surface chemistry and catalysis. The WTEC group formally met with Professor Sir David King, Dr. Stephen Jenkins, and the King/Jenkins group and Dr. Richard Lambert's group. Professor Lambert was traveling.

Professor David King and Dr. Stephen Jenkins

The King/Jenkins Surface Science Research Group (http://www-dak.ch.cam.ac.uk/) is jointly run by Professor David King and Dr. Stephen Jenkins and has strong efforts in both experiment and theory. The group has maintained a consistent level of funding of over £600,000 per year for the past two decades, with support from the Engineering and Physical Sciences Research Council (EPSRC), the Leverhulme Trust, Isaac Newton Trust, Johnson Matthey, Shell Global Solutions, BP Alternative Energy, Toyota, and DSM. The lab staff is currently comprised of 11 PhD students and 7 postdoctoral fellows.

The group combines a range of expertise in the development and application of surface characterization techniques, which include Ultrahigh Vacuum and High-Pressure Reflection-Absorption Infrared Spectroscopy (UHV-RAIRS and HP-RAIRS), Low-Temperature Scanning Tunneling Microscopy

(LT-STM), Fiber Optic Low Energy Electron Diffraction (FO-LEED), Supersonic and Molecular Beams, and Single-Crystal Adsorption Calorimetry (SCAC). Researchers in this group have recently developed a novel Fiber Optic LEED instrument and a corresponding approach to probe adsorbate-adsorbate configurations on surfaces for systems that are highly sensitive to beam damage. This approach allows them to analyze, in detail, systems that are controlled by weaker interactions, with the substrate and intermolecular hydrogen bonding along the surface without damaging the adlayer. This group also previously pioneered the development of single-crystal calorimetry, which allows for accurate heats of adsorption and surface reactivity (Ge, Kose, and King 2000). This was an important advance to provide information on the intrinsic surface adsorption energies, lateral interactions between adsorbates, and heat evolved from surface chemistry. The group began a strong theory effort in the mid 1990s to complement its experimental efforts. The theory effort has grown to be an important component of much of its efforts to complement as well as guide the experimental program.

Professor Richard Lambert

The Surface Science and Catalysis Research Group of Professor Lambert (http://www-rml.ch.cam.ac.uk/) is currently comprised of 5 postdoctoral fellows and 8 PhD students. It interacts with a number of other faculty members at Cambridge as well as with researchers in Greece, Spain, Germany, France, the United States, and the UK. Its work has been well supported by the Engineering and Physical Sciences Research Council (EPSRC), National Environmental Research Council (NERC), Johnson Matthey, BOC, and the European Union. This group has developed and used a wide range of characterization methods, which include *in situ* spectroscopy and kinetic measurements to elucidate the structure and reactivity of solid surfaces and at liquid/solid interfaces over a very wide range of conditions, spanning ultrahigh vacuum to high pressures. Group researchers have examined the surface chemistry and kinetics for a wide range of different catalytic systems. Much of their effort, however, is focused on heterogeneous catalysis and understanding the mechanisms for important classes of reactions. The group has made numerous seminal contributions to heterogeneous catalysis, surface science, and electrocatalysis over the past decade.

RESEARCH AND DEVELOPMENT

Professor King/Dr. Jenkins Group

The group currently has four major focus areas, based on past areas of expertise and future growth areas:

1. Complex Interadsorbate Interactions
2. Nanoscale Surface Phenomena
3. Chiral Surface Systems
4. Tuning Reactivity and Catalysis

The group discussed three different areas of research, which are highlighted below.

1. Chiral Surfaces and their Application to Catalysis

Chiral molecules are found throughout nature. Different enantiomers can express very different properties. Highly efficient catalytic and separation processes are then necessary in order to purify the product. One means to synthesize or separate chiral intermediates is to use chiral surfaces or create local chiral sites via chiral modifiers, since chiral molecules respond asymmetrically to chiral environments. The King/Jenkins group has been examining the intrinsic surface chemistry of chiral transition metal surfaces (Pratt, Jenkins, and King 2005). A diverse set of planes can be formed by cleaving a metal particle, thus exposing a wide range of different chiral surfaces. King/Jenkins researchers have examined closed-packed as well as more open achiral surfaces in order to compare with various different chiral surface planes, including the enantiomeric fcc {531} and hcp $\{\mathbf{41\bar{5}2}\}$ surfaces, the diamorphic $\{\mathbf{10\bar{1}0}\}$, and hcp (hexagonal closest packing) stereomorphic $\{\mathbf{21\bar{3}1}\}$ surfaces (Pratt, Jenkins, and King 2005). They have also examined the adsorption, intermolecular interactions and reactivity of four different small probe molecules of interest in

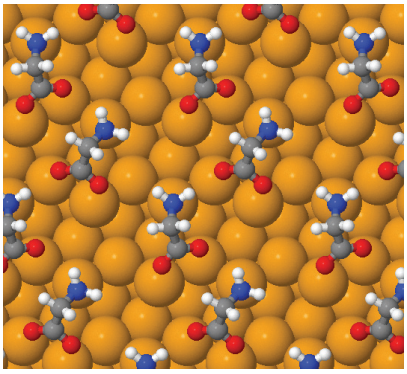

Figure D.38. DFT-calculated hemisorption of glycine on Cu{531} (courtesy of King/Jenkins group).

biology: glycine, alanine, pyruvic acid, and lactic acid. Figure D.38, for example, shows the adsorption of glycine.

2. Low-Temperature Catalysis over Noble Metals: Mesoscopic Order and Nanocluster Formation on Au(111)

Two particular examples were discussed where ultrahigh vacuum experiments were carried out together with theory to understand the nature of molecular surface interactions and their influence on metal surface chemistry. In the first system, scanning tunneling microscopy (STM) along with reflection-absorption infrared spectroscopy (RAIRS) experiments were carried out under UHV conditions to understand the unique interactions that occur between CO and NO_2 on Au{111} (Zhang et al. 2005). It is well established that CO does not chemisorb onto Au{111} above 50 K. The King/Jenkins researchers found that the coadsorption of NO_2 stabilized CO on the Au{111} for temperatures up to 145 K. NO_2 and CO surface species organize into a $(\sqrt{7} \times \sqrt{7})R19^{o}$ LEED pattern with a 3:1 NO_2 to CO stoichiometry as the result of attractive interactions between the two molecules on the surface. They found a surprising blue shift of the CO vibrational band by 43 cm^{-1} as a result of these interactions. STM studies were carried out in order to image the molecules at 5 K, thus confirming the $(\sqrt{7} \times \sqrt{7})R19^{o}$ structure. The resulting STM images are shown in Figure D.39. The NO_2 molecules appear as bright spots and maxima; the CO molecules are the darker and subsidiary maximum. DFT calculations were used to help confirm the structure. Subsequent calculations were carried out to determine the density of states and simulate the STM images. The theoretically simulated STM and the actual STM were found to be in very good agreement (Zhang et al. 2005).

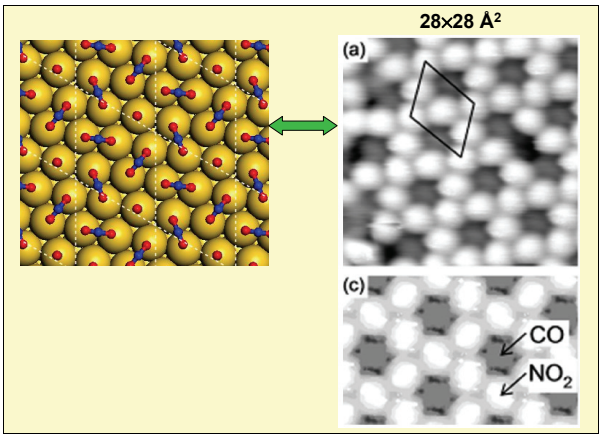

Figure D.39. Coadsorption of NO_2 with CO results in the formation of a $(\sqrt{7} \times \sqrt{7})R19^{o}$ structure. The experimental STM structure is shown on the right-hand side. It is in excellent agreement with the DFT predictions of the lowest energy NO_2/CO structure on Au{111} arrangement shown on the left-hand side (Zhang et al. 2005).

Group researchers also used theory to help establish the electronic factors that govern the attractive interactions between coadsorbed NO_2 and CO. A detailed analysis of the changes in the charge distribution upon co-adsorption of CO and NO_2 indicate that there is a depletion of electron density from the CO $2\pi^*$ state, which strengthens the C=O bond, and an increase in the electron density in the 5σ M-CO and the $6a_1$ M-NO_2 states, which weaken the metal-CO bond and strengthen the metal-NO_2 bond, respectively. The monopole and dipole interactions demonstrate weak attractive interactions, which act to control the chemisorption to the surface. The depletion of electron density from the CO $2\pi^*$ state leads to a blue shift in the C-O frequency, whereas the increase in electron density in the 5σ state results in a red shift. The $2\pi^*$ state

is more antibonding; as such, the blue shift wins out. In addition, there are electrostatic restoring forces due to the coadsorption of NO_2, which also enhance the blue shift. The key result is that since the adsorption between the CO and the metal is weak, all other possible interactions must be examined in detail, because their small effects can result in important changes.

In a second example, this group has demonstrated how the adsorption and lateral interactions that occur between molecules on the surface can lead to unique changes in the surface structure (Driver, Zhang, and King 2007). NO_2 was adsorbed to the Au{111} surface at increasing surface coverages. The clean Au{111} surface is known to undergo a herringbone reconstruction. Upon the adsorption of NO_2 there is a uniaxial lateral contraction as a result of the formation of stress domains that build up in the adsorbate region, which leads to a loss of registry of the surface. Alternating fcc (face centered cubic) and hcp stacking phases result, leading to the formation of stripes along the surface. These regions are separated by soliton walls, which are the bright lines in Figure D.40A.

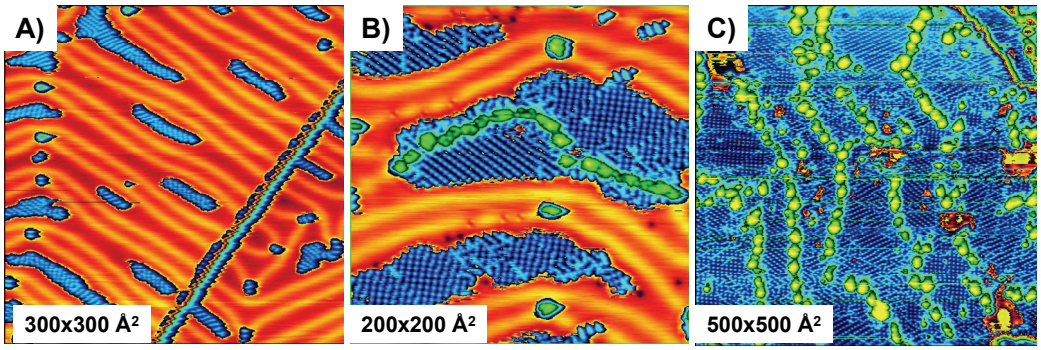

Figure D.40. STM images of the changes in the surface structure as a function of NO_2 coverage: (A) Low coverage adsorption of NO_2 show NO_2 islanding which results in lateral bowing of soliton walls. (B) Increasing NO_2 coverage results in local lifting of reconstruction and ejection of Au atoms. (C) Saturation coverages of NO_2 result in massive reconstruction, further resulting in complete lifting reconstruction and formation of nanocluster Au strings locked into initial positions (Driver, Zhang, and King 2007).

"Elbow" patterns in the walls exist at domain boundaries; these are threading dislocation sites. The initial exposure of the clean surface to NO_2 leads to the formation islands on the fcc stripes comprised of NO_2 aggregates. There is a lateral bowing of the soliton wall as a result of the compressive stress fields that form around the islands. The resulting pattern and stress field lead to the mesoscopic ordering shown in Figure D.40B. At higher NO_2 coverages, adjacent islands begin to aggregate and cover up hcp regions. There is a local lifting of the herringbone reconstruction, and as a result, excess Au atoms are locally released from the soliton walls. The Au atoms have little time to diffuse away; instead, they begin to form nanoclusters or strings of Au at the points where they have been ejected. This is shown in the "S bend structures" seen in Figure D.40B (green horizontal curved "chain" above the center of the image). This local reconstruction can lead to massive cooperative restructuring of the surface. At NO_2 saturation coverages, the herringbone reconstruction is completely lifted as the surface is covered in NO_2. Local Au nanocluster strings are subsequently locked into their initial positions, as shown in Figure D.40C (in green or lighter color vertical "chains"). This system nicely demonstrates how chemisorption and lateral interactions can lead to significant reconstructions and, in particular, result in the formation of nanoscale Au islands (Driver, Zhang, and King 2007). The work is being continued with the hope of exploiting the nanoparticles of Au to carry out water gas shift catalysis for H_2 production.

3. Theoretical Studies on the Influence of Alloying Rh for DeNO$_x$

Density functional theoretical calculations were carried out to follow the dissociation of NO over model Rh{111} and Rh3Ag{111} and Rh{211} and Rh3Ag{211} surfaces in order to understand the influence of Ag (Inderwildi, Jenkins, and King 2007). The results indicate that the Rh atoms adjacent to Ag regions are the active sites. Both electronic and strain effects appear to be important in influencing NO dissociation.

Subsequent efforts examined ternary alloys and found that the Rh{211}AgCu surface leads to reduced adsorption of NO, along with a lower activation barrier. The stability of the alloy and the specific location of the metals are currently being explored.

Professor Lambert's Group

The current interests of the group include

- Photocatalysis
- Solid State Electrochemistry
- Surface-Mounted Molecular Rotors
- Sensors
- Enantioselective and Chemoselective Reactions
- New Approaches to 2D Molecular Self-Assembly
- Biomimetically Inspired Catalytic Systems Based on Tethered Metalloporphyrins
- Heterogeneous Chemistry of Tropospheric Mineral Aerosols

The research discussions with the WTEC team were focused on some very recent work from the Lambert group in three new areas of research:

1. Biomimetically Inspired Catalytic Systems
2. Epoxidation Catalysis over Nanoparticles of Au
3. Asymmetric Hydrogenation

1. Biomimetically Inspired Catalytic Systems

Nature is known to be quite effective in carrying out reactions with unprecedented selectivity and activity. While there have been significant efforts to mimic the active features of enzymes, many of these systems are unstable. The Lambert group has recently established a strong effort at synthesizing, characterizing, and stabilizing adsorbed active biomimetic systems onto metal substrates that can effectively promote the active centers (Vaughan, Williams, et al. 2006; Williams et al. 2004; Vaughan et al. 2004; Vaughan, Turner, et al. 2006). Group researchers have described in detail their efforts on the synthesis of reactivity of biomimetic epoxidation catalysts. The epoxidation of ethylene is carried out commercially over Ag supported on Al_2O_3 in a process that offers a relatively high yield of ethylene epoxide. Ethylene adsorbs weakly to Ag and subsequently reacts with atomic oxygen that forms as the result of the activation of O_2. The epoxidation of higher alkenes, however, is much more difficult as the result of the allylic hydrogen atoms being more readily extracted, thus resulting in significantly lower selectivities. There are no clear commercial catalysts that can achieve the yields found for ethylene. This group has recently sought to develop two novel approaches. The first involves the synthesis and application of biomimetic heterogeneous catalysts; the second involves catalysis by gold nanoparticles.

Nature is highly active and selective in carrying out a wide variety of oxidation reactions. Development of homogeneous metalloporphyrin catalysts that mimic the active site in cytochrome P450 has been quite successful, resulting in very high yields and selectivities. The catalytic cycle, however, requires atomic oxygen and/or the aid of a sacrificial reductant. Such systems pose environmental concerns and are quite costly.

The Lambert group's goal is to functionalize homogeneous bio-mimetic organometallic systems onto Ag surfaces in a controlled manner to establish highly active and selective heterogeneous catalysts. Ag will be used to adsorb the olefin and, more importantly, to activate molecular oxygen to supply the active site of the metalloporphyrin to carry out the epoxidation. Ag is also used, as it results in weaker interactions with the porphyrin system. This should help to keep the porphyrin well dispersed on the surface and prevent it from blocking sites for O_2 activation on the surface. Figure D.41 shows this conceptually. The work involves

significant effort in (1) synthesis of novel and relevant metalloporphyrins, (2) model studies and surface characterization of deposited porphyrins under ultrahigh-vacuum conditions, and (3) development of practical dispersed catalysts.

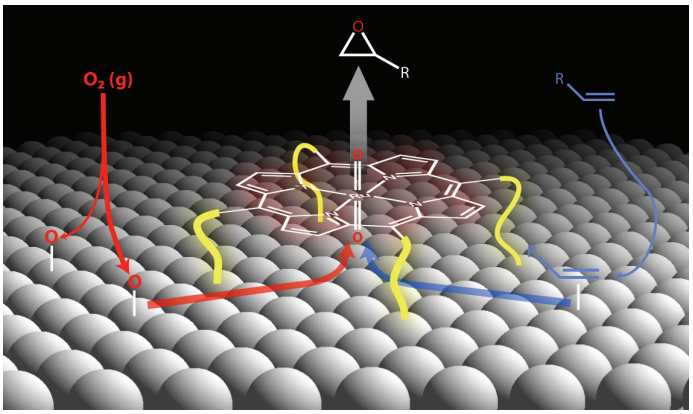

Figure D.41. Schematic of Ag{111} surface functionalized with metalloporphyrin. Ag is used to adsorb the alkene and activate O2 and supply the alkene along with reactive atomic oxygen to the attached porphyrin to carry out the epoxidation (courtesy of the Lambert group).

The Lambert group researchers have developed a refined synthesis strategy that allows them to readily isolate pure porphyrin systems with good yields. This was demonstrated for the synthesis of $Ru^{VI}(O)_2$TBPP (tetra-3,5-di-ter-butyl-phenyl porphyrin) (Williams et al. 2004; Vaughan et al. 2004).

In the second step, the group successfully deposited Zn-TBPP onto the Au(100) surface by use of a source temperature for the porphyrin of 523 K and an Ag(100) surface temperature of 298 K (Williams et al. 2004; Vaughan et al. 2004). The surface was then annealed to 523 K for 60 minutes. STM images established the porphyrin structure and its specific arrangements and coverage on the surface. The STM image of the Zn-TBPP displays four characteristic bright spots arranged in a square. These "lobes" are from the four TBP ligands, which are oriented perpendicular to the plane of the porphyrin and sit vertical with respect to the surface. This is shown in Figure D.42A.

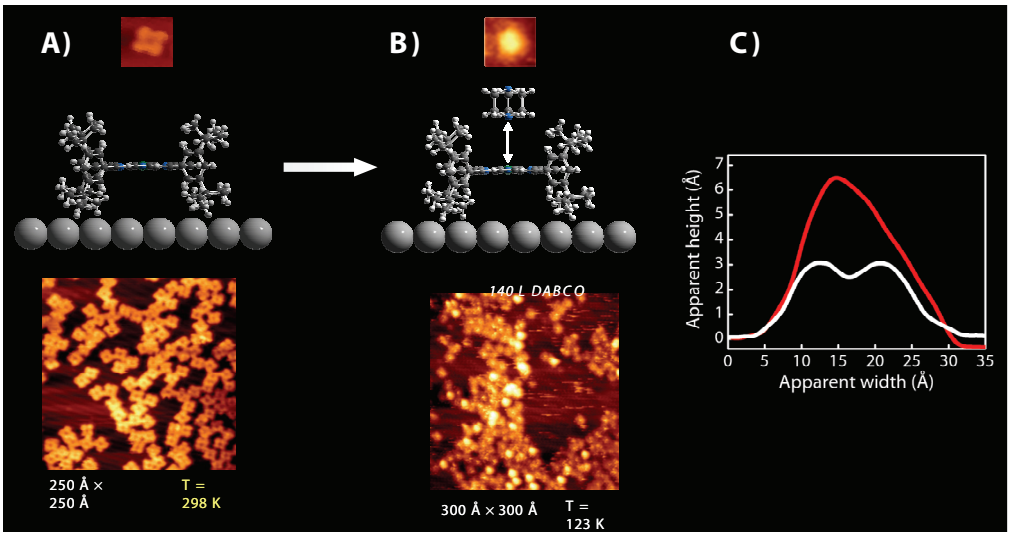

Figure D.42. STM images showing the effects of the addition of DABCO on the adsorption of Zn-TBPP molecules on Ag{100}. The 4 characteristic lobes that correspond to the TBP ligands are seen quite clearly. The uncapped system has two characteristic peak widths and a lower height. The DABCO capped system has one central peak that is higher than the uncapped (Williams et al. 2004; Vaughan et al. 2004).

The ligand 1,4, diazabicyclo (2,2) octane (DABCO) is added to a wide range of porphyrin homogeneous catalytic systems to form supramolecular complexes that aid in epoxidation. The Lambert group showed that the addition of DABCO could be used to establish ligated Zn-TBPP(DABCO) surface porphyrins. The system results in a capping of the Zn-TBPP, which can be readily added or removed similar to chemistry of homogenous catalytic systems, and thus acts as an effective ligand. This is shown very nicely in the STM images in Figure D.42B. The uncapped system has a square arrangement of 4 distinct "lobes" that reveal the tetra butyl phenyl groups (Figure D.42A). The square bright spots refer to the capped system. The uncapped system has two maxima in height where the TBP groups lie and is about half the height of the capped system, which due to the DABCO cap has just one major peak, as is seen in Figure D.42B. The addition of DABCO at low temperature caps the Zn-TBPP. Increasing the temperature to room temperature removes the ligand (Williams et al. 2004; Vaughan et al. 2004).

In moving from the monofunctional DABCO ligand to a difunctional 4 methoxypyridene, the Lambert group created a surface mounted rotor (Vaughan, Williams et al. 2006). The 4 methoxypyridene binds to the surface beneath the TBPP and attaches to the TBPP, thus acting as an axle. TBPP rotates along the axle on the time frame of the experiment. This is seen in examining the STM figure shown in Figure D.43, which shows that the 4-lobed features of the adsorbed TBPP are reduced to toroidal features. By carefully choosing the binding between the wheel (TBPP) and the axle (4 methoxypyridene), they hope to create systems that switch at different temperatures. Lower temperatures should allow the system to spin; this could lead to catalytic behavior that can be switched on and off.

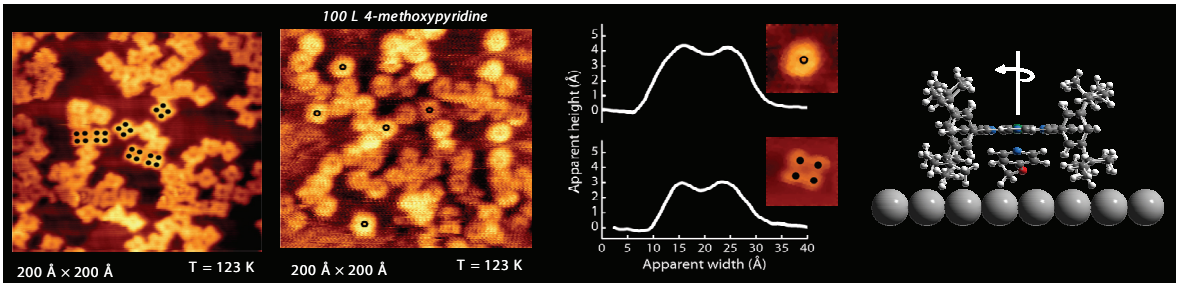

Figure D.43. STM images showing the effects of the addition of 4 methoxypyridene on the adsorption of Zn-TBPP molecules on Ag{100}. The 4-lobal Zn-TBPP disappears and there a toroidal structure forms. The methoxypyridine acts as an axle to which the Zn-TBPP attaches to the surface. The Zn-TBPP can than rotate freely about the axle (Vaughan, Williams, et al. 2006).

The two porphyrin/Ag systems discussed are both physisorbed systems that lack the covalent attachment of the porphyrin complex to the metal. As such, they are likely to readily degrade and thus are very limited. In more recent work, group members have demonstrated the ability to control surface-mediated deprotection of thioacetyl groups in order to covalently tether thiol terminated porphyrins to the Ag(100) surface (Vaughan, Turner et al. 2006). The deposition of tetra(thioacetyl) porphyrin, [Sac]4P-H2, onto Ag(100) under vacuum conditions resulted in the formation of aggregates that could then be covalently tethered to the surface by heating to higher temperatures. This was directly seen using STM spectroscopy. The mechanism involved the acetyl cleavage by the surface, resulting in the formation of a porphyrin strongly tethered to the surface. They showed that the addition of oxygen at $5x10^{-8}$ mbar at 298 K resulted in highly dispersed and deprotected surface porphyrin intermediates. Heating to 325 K led to the complete dispersion of the covalently tethered porphyrins and the removal of the acetyl species from the surface. The dispersion of the porphyrins as the result of the exposure to oxygen could be due to oxidation of the sulfur from S^{IV} to S^{VI}, which weakens the metal-sulfur (M-S) bond. Their ability to apply protected thiol species to a metal surface and subsequently deprotect them via vapor deposition may be useful in preparing a wide range of other functionalized catalysts as well.

2. Heterogeneous Catalyzed Asymmetric Selective Hydrogenation

The Lambert group has also been working actively in the area of heterogeneous asymmetric hydrogenation catalysis since about the year 2000 (see list of publications in this topic area in the References section of this

site report). They have used both single crystal ultrahigh-vacuum studies as well as actual reactions over metal surfaces in solution to understand the nature of how different multifunctional oxygenated molecules and their reaction intermediates adsorb and react on different metal surfaces. This group has provided quite detailed analytical characterization and kinetic analysis in order to help resolve the mechanisms that govern the surface chemistry and establish structure sensitivity for these reactions. They presented recent results on the asymmetric hydrogenation of C=C bonds. More specifically, they discussed results for the enantioselective hydrogenation of isophorone with the addition of proline as a directing agent over Pd supported on carbon to form 3,3,5 trimethyl cyclohexanone (TMCH). This catalyst was previously shown in the literature to lead to the highest enantiomeric excess ratios of 51% and TMCH yields of 27%. Previous experimental studies suggested that the intermediates formed from the condensation of proline and isophorone were important reaction intermediates, and their subsequent reactions controlled the rates and selectivity (McIntosh, Watson, and Lambert 2007).

Through detailed gas chromatography (GC), high-pressure liquid chromatography (HPLC), and ultraviolet visible UV-Vis spectroscopy of the reaction products and careful kinetic experiments, researchers in this group were able to establish a rather complete picture of the controlling reaction mechanism and conclusively demonstrate that previous speculations about the mechanism were incorrect. While the proline-isophorone condensation intermediates do form, they are purely spectator intermediates. The enantioselectivity is controlled by *kinetic resolution*, which involves homogeneous kinetics rather than metal catalysis. TMCH is readily produced by the hydrogenation of isophorone to form a racemic mixture. Proline subsequently reacts in the solution phase very rapidly with one of the isomers; it reacts much more slowly with the other, thus leaving an enantiomeric excess of the favored isomer in solution. Although the metal surface is involved in carrying out the initial hydrogenation reaction, it is not involved in the rate-determining step. This is quite different than what is known for the mechanisms involved in the asymmetric hydrogenation of ketoesters. Their mechanism for the asymmetric hydrogenation of isophorone helps to explain all of the intermediates that are formed in this complicated system as well as the fact that there is a maximum in attainable enantiomeric excess (ee) at about 50% (McIntosh, Watson, and Lambert 2007).

These researchers are currently working on the development of novel asymmetric hydrogenation promoters that can be strongly anchored to the surface throughout reaction yet avoid blocking access of the reactants to the surface. They discussed the synthesis and kinetics for a wide range on novel surface ligands, which include amino acids, Macmillan type, Jorgenson type, modified proline, and thiol modified proline for promoting the asymmetric hydrogenation of ethyl pyruvate to ethyl lactated over supported Pt. The thiol modified proline ligands appeared to provide the best ee values. In addition, they were able to show that largest “steric” type ligands showed the best ee values, whereas the largest aromatic ligands showed no ee.

In current efforts they are collaborating with Professor Chris Baddeley from St. Andrews University to carry out *in situ* STM to examine whether the ligands form self-assembled monolayers and *in situ* infrared measurements to help elucidate the mechanism occurring on the surface in solution.

SUMMARY AND CONCLUSIONS

The work in both the King/Jenkins and Lambert laboratories has pioneered the development and application of surface science methods and their application under working conditions to examine surface chemistry and catalysis for a wide range of catalytic systems. The King/Jenkins group has elegantly combined surface science together with theory to provide a critical understanding of the nature of adsorbate-adsorbate interactions and how they influence surface chemistry and impact catalysis over different metals and alloys. The Lambert group has effectively combined surface science studies with actual catalytic studies, and it collaborates with theoreticians in order to provide an in-depth understanding of the mechanisms for a wide range of catalytic systems. Both groups are extending these efforts towards the design of novel catalytic systems.

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Site: **University of Cambridge Magnetic Resonance Research Centre**
Magnetic Resonance and Catalysis Group
Department of Chemical Engineering
New Museums Site
Pembroke Street
Cambridge, UK CB2 3RA

Date Visited: September 28, 2007

WTEC Attendees: L. Thompson (report author), J. Miller, J. Regalbuto, M. DeHaemer

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BACKGROUND

The University of Cambridge's Magnetic Resonance Research Centre (MRRC) was built in 1997 on the West Cambridge Site near the Cavendish Laboratory. This facility acts as a focus for academic and industrial researchers throughout the United Kingdom to apply magnetic resonance techniques to problems in chemical engineering. These problems scale from understanding the molecular level function of nanostructured catalysts to determining flow patterns in reactors (see Figure D.44).

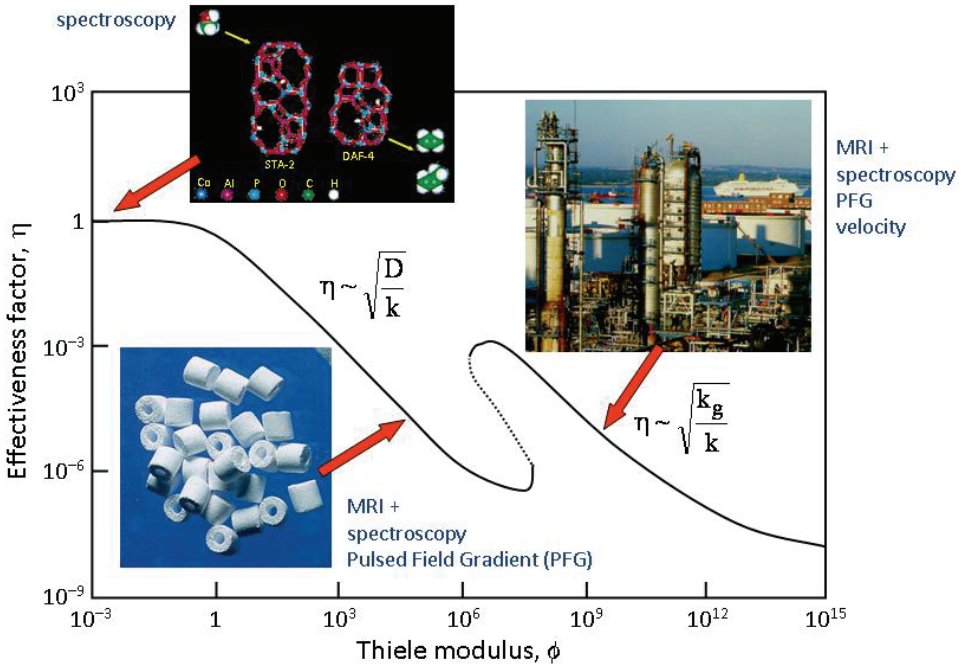

Figure D.44. Schematic illustrating the range of scale for the application of magnetic resonance tools to catalysis and reaction engineering issues.

The Magnetic Resonance Research Centre houses four Bruker NMR spectrometers to perform NMR spectroscopy, diffusion, imaging, and flow visualization experiments:

1. Bruker AV400 WB: ^{1}H microimaging and solid state MAS NMR spectroscopy
2. Bruker DMX 200 SWB: microimaging and flow imaging (^{1}H, ^{13}C, ^{2}H, ^{31}P, ^{23}Na, ^{7}Li, ^{19}F, ^{14}N)

3. Bruker DMX 300 WB: pulsed field gradient and microimaging (^{1}H, ^{13}C, ^{2}H, ^{31}P, ^{23}Na, ^{7}Li, ^{19}F, ^{14}N)
4. Bruker AV85 (horizontal bore size 30 cm)

These instruments were acquired using funds from the Engineering and Physical Sciences Research Council (EPSRC) and industrial sponsors. The 85 MHZ instrument was acquired through collaboration with Schlumberger for studying multiphase flow in rock cores.

Current projects focus on the development of ultrafast magnetic resonance imaging (MRI) techniques to capture images of hydrodynamics and the spatial variation of concentration in chemical reactive flows. Resolution is typically 30-500 μm, although it is hoped to increase this by an order of magnitude. A new direction is to extend into THz (vibrational) spectroscopy and imaging. To this end, a combined THz/MRI measurement system is currently being constructed.

The facility has two full-time assistant research directors and accommodates approximately 30 visitors, including 3 from academia. The operating budget is approximately £1 million, of which approximately 60% comes from EPSRC and the balance from industrial grants. Some of the funding is provided via collaborations in major UK-based catalysis consortia, namely ATHENA and CARMAC. ATHENA is funded by EPRCS and Johnson Matthey, and has partners from University of Birmingham, University of Cambridge, University of Cardiff, Fritz-Haber-Institute, Northwestern University, University of Surrey, and Johnson Matthey. CARMAC is a Center for Reaction Engineering and the Technology of Reaction (CREATOR), and has collaborations between Queen's University Belfast, University of Cambridge, University of Virginia, University of Reading, Johnson Matthey Catalysts, Robinson Brothers, and Grace GmbH and Co. The effort is jointly sponsored by EPSRC and several industrial partners (£5 million over five years).

RESEARCH AND DEVELOPMENT

The MRRC is using magnetic resonance techniques to characterize multiphase flow in porous media, solids fluidization, catalytic materials, and pharmaceutical and agrochemical controlled release technology (refer to references at end of this site report for examples of publications). Flow distributions are imaged in reactor environments such as monoliths and fixed beds. Figure D.45 highlights use of our ultra-fast imaging techniques to study turbulent flow in a pipe (Sederman et al. 2004).

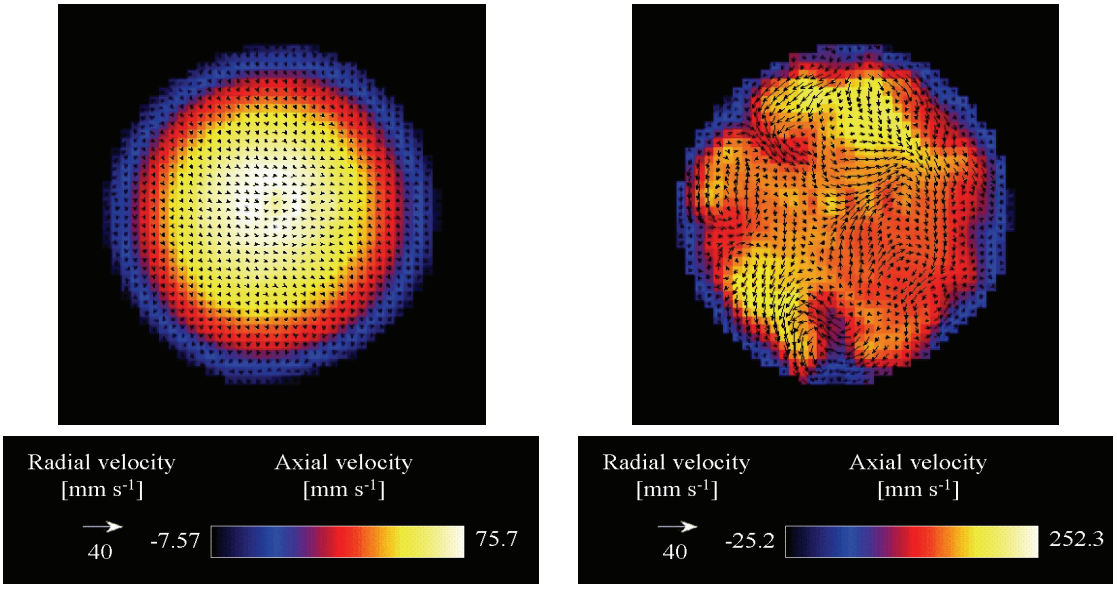

Figure D.45. Magnetic resonance images of velocity profile in a ceramic monolith catalyst acquired for varying Reynolds numbers. The pipe diameter is 29 mm.

In other examples, chemical characterization and imaging are combined to produce maps of chemical conversion along the length of a reactor. As illustrated in Figure D.46, the distributions of octenes and octane can be resolved using the ^{13}C spectra. Increase in formation of 3- and 4-octenes increases as the hydrogen flow rate is increased. These types of results could guide catalyst placement in the reactor.

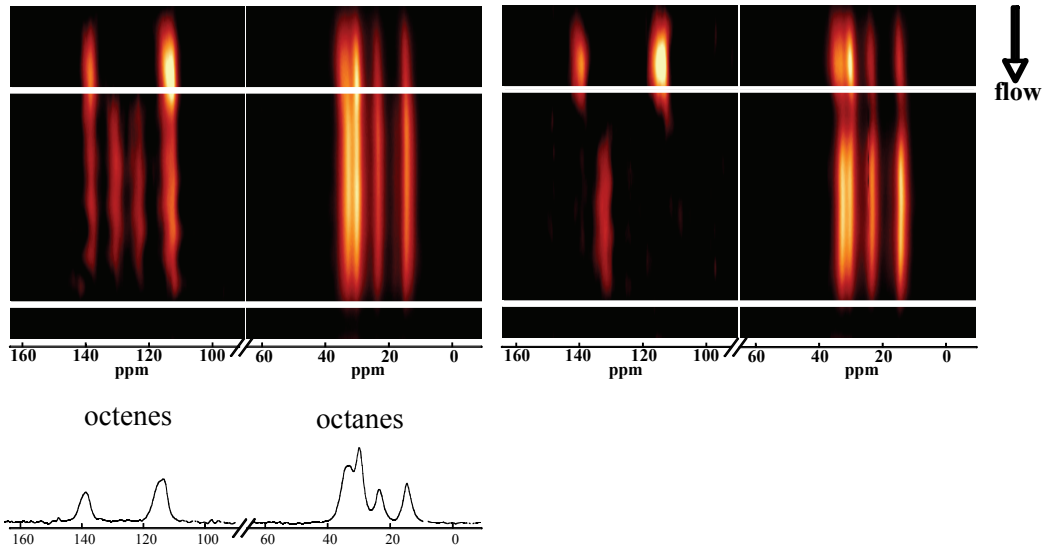

Figure D.46. Chemical maps for 1-, 2-, 3- and 4- octene, and octane during the hydrogenation of 1-octene at (a) low and (b) high H_2 flow rates.

In a final set of examples, the deactivation of catalysts is characterized *in situ* using magnetic resonance spectroscopy. Figure D.47 illustrates variations in the amount of valeronitrile produced during the hydrogenation of trans-3, pentenenitrile. The cumulative conversion increases as one moves down the bed, indicating that catalysts at the entrance deactivate more quickly than catalysts at the exit.

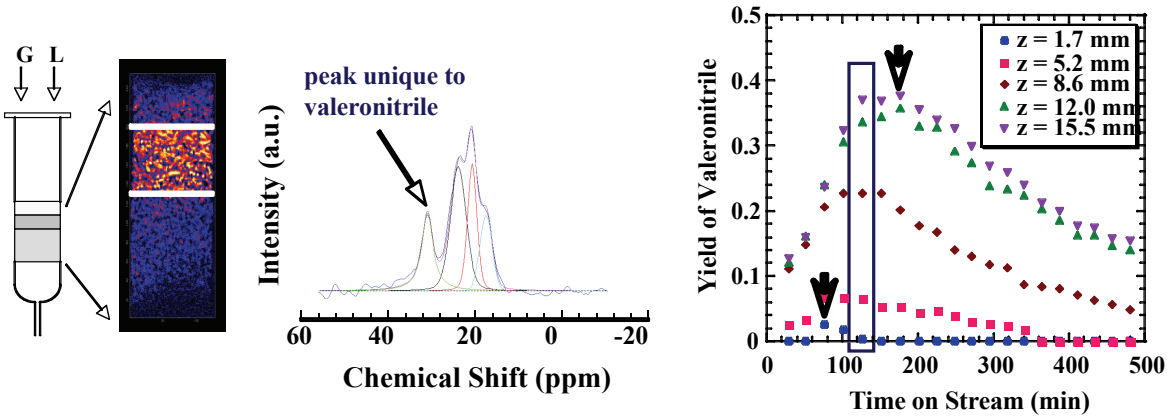

Figure D.47. Characterization of the deactivation of a trans-3, pentenenitrile hydrogenation catalyst as a function of position in the bed.

SUMMARY AND CONCLUSIONS

The MRRC is a tremendous facility for the characterization of catalysts and reactor systems. Work being carried out at the MRRC is not only advancing our understanding of the coupling between flow and hydrodynamics, it is advancing the development of magnetic resonance tools for use in chemistry and

chemical engineering research. Funding for research is substantial and supports a large number of researchers, the necessary equipment, and infrastructure. The results of research are disseminated via seminars, journal articles, monographs, and patents. There is also a track regard of translation of the research findings into innovations via collaborations with industrial and industrial consortia.

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Site: **University of Messina and University of Turin: Interuniversity Initiatives in Italy on Catalysis by Nanostructured Materials**
Interuniversity Consortium on Science and Technology of Materials (INSTM)
Integrated Design of Catalytic Nanomaterials for Sustainable Production (IDECAT)
European Laboratory of Catalysis and Surface Science (ELCASS)

Date Visited: September 24, 2007

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BACKGROUND

During a full-day workshop at the University of Turin, the WTEC visiting team met with representatives from several Italian institutions involved in catalysis research and development. This site report covers discussions the team had with representatives from institutions in Messina and Turin and Italy's consortia supporting R&D on catalysis.

Much of the catalysis research in Italy is coordinated through multiuniversity initiatives and is funded by European contracts. Support for all European-funded projects in the area of nanomaterials have totaled approximately €65 million, of which about €10 million support or have supported activities in the Network of Excellence (NoE) over the years 2005–2010, about €8 million support or have supported integrated projects (also over 5 years), and about €4–5 million support or have supported small research projects (over 3 years).

Italy's Interuniversity Consortium on Science and Technology of Materials (INSTM) was established to promote, coordinate, and perform materials science research in Italy with a particular focus on chemistry, engineering, and nanotechnology. The INSTM also provides a single reference point for international partnerships and collaborations and access by industry to consultants. Finally, the INSTM promotes formation of centers of excellence and major user facilities to perform materials science research. All 44 universities in Italy are affiliated with the INSTM; its total annual increased from just over €5 million in 2000 to more than €28 million in 2006; it appears that at that time, approximately €1.3 million was devoted to catalysis research. Approximately 60% of the funding derives from EU contracts, ~30% from the Italian government, and ~10% from industrial contracts. Professor G. Centi serves on the Scientific Council.

The INSTM comprises eight thematic sections; most of the catalysis research is performed as part of Section 3, Surfaces, Thin Layers and Interphases. There are two INSTM research centers focused on catalytic materials (of a total of 15 nationwide), each funded at approximately €0.5 million:

- Laboratory of Catalysis for a Sustainable Production and Energy (CASPE) (coordinated by Professor G. Centi, University of Messina)
- Nanostructured Interphases and Surfaces (NIS), Large Surface Extension Materials (coordinated by Professor A. Zecchina, University of Turin)

Figure D.48. University participants in the INSTM.

Catalysis research in Italy is also accomplished in connection with two European Union-wide initiatives. The first is *Integrated Design of Catalytic Nanomaterials for Sustainable Production (IDECAT;* http://idecat.unime.it/). This is a European Network of Excellence (NoE) program with funding of €9.5 million for a 5-year period begun in 2005. The NoE was established to strengthen Europe's science and technology excellence through integration of research capacities of its participants. The architecture for the IDECAT is illustrated in Figure D.49. Support from the NoE is solely for integration activities. The IDECAT includes 37 laboratories from 17 institutions and 12 countries. More than 500 researchers participate in the IDECAT. There are several Italian participants, including the University of Turin's Chemistry IFM Department.

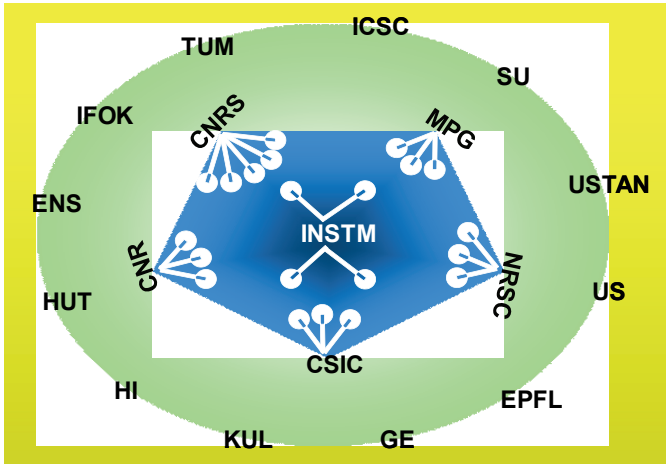

Figure D.49. Illustration of the organizations and countries involved in the EU's IDECAT program (courtesy of G. Centi).

Research in the IDECAT NoE on Catalysis focuses on the rational synthesis of nanoscale objects and the integrated design of catalytic nanomaterials to achieve nonevolutionary and knowledge-based development. Examples of ongoing projects include

- Nanoporous materials as tailored reactions space
- Nanofibrous materials as catalysts and supports
- Robust non-leaching supported catalysts
- Dendrimers and supported enzymes
- New single site catalysts, activators, and composite materials
- Ionic liquids
- Chemicals from renewables
- Photocatalysis
- New nanostructured catalysts for low-temperature fuel cells

The second European Union-wide catalysis initiative is the *European Laboratory of Catalysis and Surface Science (ELCASS)*, a virtual institute linking the University of Messina (UNIME), Centre National de Recherche Scientifique (CRNS), Université Louis Pasteur (ULP), and Max-Planck-Gesellschaft, Fritz-Haber-Institute (MPG-FHI). Current directors of the ELCASS are Drs. G. Centi, M.J. Ledoux, and R. Schlögl. ELCASS research combines fundamental and applied aspects of nanomaterials for catalytic applications; it is financially supported (over 60%) by bilateral contracts with companies or EU research contracts.

RESEARCH AND DEVELOPMENT

University of Messina (UNIME)

Programs at UNIME that are supported by the ELCASS include research on nano-carbon-based catalysts, the conversion of CO_2, and nanostructured photocatalysts. These programs involve four research groups and approximately 30 students. Mesoporous carbon (SBA-15)/carbon cloth composites are being impregnated with Co and Fe to produce fuel cell electrocatalysts. Carbon nanotube and nanofiber support Pt and Pt-Ru electrocatalysts are being developed for use in proton exchange membrane (PEM) fuel cells. The physical nature and chemical nature of the Pt clusters were significantly affected by the nature of the carbon support. The nanofiber-supported catalysts had higher current densities than a commercial 20 wt% Pt/C electrocatalyst from E-TEK. A Pt-Ru/MWCNT was also reported to be more tolerant to CO then a commercial Pt-Ru/C electrocatalyst from E-TEK. One of the more intriguing projects involved the electrocatalytic conversion of CO_2 into fuels (Centi et al. 2007a). These experiments are carried out in a modified proton exchange membrane fuel cell. Long chain hydrocarbons and alcohols could be produced with efficiencies near 30% under ambient conditions (see Figure 6.18). Catalysis research at UNIME also includes the following:

- Conversion of renewable resources
  - upgrading bioethanol to diesel components
  - hydrolysis of lignocellulose
- Production and conversion of hydrogen
  - low-temperature photocatalytic hydrolysis of lignocellulose
  - thin Pd membranes on ceramic substrates for use in low-temperature (500°C) methane steam reforming reactors
- Cleaner process routes
  - Direct synthesis of H_2O_2 from H_2 and O_2 in CO_2-expanded solvents
  - Catalytic treatment of effluents from agro-food production
- Photoactive materials
  - Titania nanocoils and photonic crystals (Centi et al. 2007b and 2007c)
  - Development of nanostructured, doped titania thin films
  - Hydrogen production from water and from biomass

University of Turin (Università di Torino), Department of Chemistry IFM Centre of Excellence "Nanostructured Surfaces and Interfaces" (NIS)

Heterogeneous catalysis, photoactive surfaces, and microporous materials research and development in the INSTM is performed as part of the Surfaces, Thin Layers, and Interphases thematic section of the University of Turin's Department of [Inorganic, Physical, and Materials—"IFM"] Chemistry Centre of Excellence program entitled Nanostructured Interfaces and Surfaces (NIS). The NIS has the mission of pursuing basic research and offering applied research services. Research lines include

- Materials and surface modeling
- Surface chemistry
- Adsorption, activation and storage of hydrogen
- Nanostructured catalysts
- Photoactive materials and molecules

Activities of the NIS are supported by nearly €3.5 million/year. Of this funding most is used on equipment and infrastructure, although approximately 25 graduate students are supported. There has been significant work in the development of characterization methods such as *in situ* Raman spectroscopy. An important activity within the NIS is the exchange of ideas via specialized colloquia with approximately 70 participants. Topics for colloquia have included

- Ab Initio Simulation of the Properties of Crystalline Surfaces and Interfaces: Progress and Prospects (May 19-20, 2005)
- Role of Surface and Interfaces in Photocatalysis: A Multidisciplinary Approach (May 30-31, 2005)
- State of the Art in Zeolite Catalysis (October 28-29, 2005)
- Raman Spectroscopy: A Powerful Technique to Characterize Nano-Materials (June 9, 2006)
- Olefin Polymerization Heterogeneous and Homogeneous Catalysts: Structure-Activity-Selectivity Relationship (October 5-6, 2006)
- Metal Organic Frameworks: Smart Materials for Catalysis and Adsorption (February 15, 2007)

SUMMARY AND CONCLUSIONS

Catalysis is a priority area for Italy and as such, research in this area is highly coordinated. This appears to be a characteristic of most high-priority academic research in the country. Research on nanostructured catalytic materials is distributed among all 44 universities, and there appear to be excellent working relationships between the various institutions. Funding for research appears to be sufficient to support a large number of researchers and the necessary equipment and infrastructure. The results of research are disseminated via a coordinated series of colloquia, journal articles, monographs, and patents. There is good evidence of the translation of research findings into innovations, including the launch of start-up companies.

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BACKGROUND

The Laboratoire de Réactivité de Surface (LRS) of the Université Pierre et Marie Curie[10] is affiliated with France's Centre National de la Recherche Scientifique (National Center for Scientific Research, CNRS). It focuses *on elaboration and functionalization of* inorganic catalytic materials and developing strategies to control their reactivity. An integrated approach is used with researchers working in four thematic groups:

I. Molecular Approach of Synthesis and Reactivity of Inorganic Materials (M. Che)

II. Synthesis and Reactivity of Nanoparticles on Oxides of Controlled Porosity (C. Louis)

III. Reactivity of Noble Metals and Carbides: Application to the Environment (G. Djéga-Mariadassou)

IV. Reactivity of Metal and Oxide Surfaces in Biological Media (J.F. Lambert and C.M. Pradier)

Research in the LRS is carried out by approximately 9 CNRS researchers, 19 professors and assistant professors, 12.5 engineers/technicians, 6 post-doctoral scholars, and 18 PhD students. Financial support for the work totals nearly € 3.5 million annually, including salaries for permanent researchers and part of the PhD students; funding for equipment and operating costs are originating as follows: 18% is provided by the CNRS and the university, 9% comes from EU contracts, 31% is derived from public agencies, and 24% is contracted from industry. The University of Pierre and Marie Curie does not have an *engineering program; therefore, the LRS often collaborates with local engineering universities*. The LRS has substantial research facilities, including several electron microscopes, an ultrahigh vacuum surface science rig capable of handling single crystals and powder materials and facilities for *in situ* infrared spectroscopy, Raman/X-ray absorption spectroscopy, EPR spectroscopy, and photoluminescense spectroscopy. Most of these facilities are maintained and operated by engineers and technicians.

[10] There were thirteen successor universities to the original branches of the ancient University of Paris; the University of Pierre and Marie Curie is one of those and is often referred to by its number as "Université Paris 6" or simply "Paris 6."

RESEARCH AND DEVELOPMENT

Research in Group I (http://www.labos.upmc.fr/umr7609/pages/theme1.htm) focuses on characterizing interactions between the solvent, precursor, and support during catalyst preparation. Results from one project indicate the precursor-promoted dissolution of support materials. For example, molybdate species have been reported to leach Al^{3+} from the surface of Al_2O_3. The resulting species can then adsorb to the support producing surface sites as illustrated in Figure D.50. This dissolution-deposition phenomena could have a significant influence on catalytic properties of the materials.

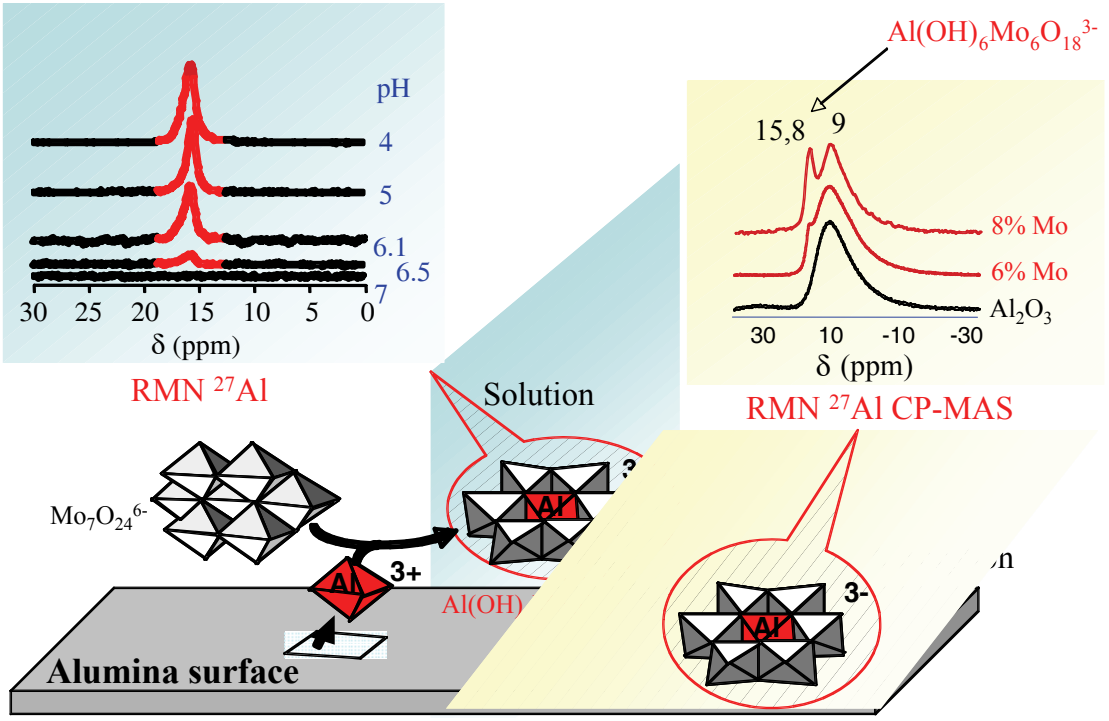

Figure D.50. Schematic illustration and associated Raman spectra indicating the dissolution of Al^{3+} and subsequent deposition of $Al(OH)_6Mo_6O_{18}^{3-}$ on the Al_2O_3 surface.

In another project, ligands or counter-ions on the precursors are being systematically varied to explore their influence on the structural and chemical properties of supported catalysts. The interactions are being characterized using ultraviolet and temperature programmed reduction spectroscopies, transmission electron microscopy, and x-ray diffraction. The final project involves an investigation of solid base catalysts with a particular focus on determining the basicities of various oxygen sites on basic oxides like MgO. In addition to reactivity probes such as 2-methyl-3-butyn-2-ol (MBOH) decomposition, the properties of various surface sites (Figure D.51) are being characterized using infrared and NMR spectroscopies.

Research in Group II (http://www.labos.upmc.fr/umr7609/pages/theme2.htm) focuses on metals on micro- and mesoporous supports and supported gold catalysts. Much of the work involves the use of *in situ* x-ray absorption spectroscopy. For example, the chemical and structural properties of Ni on NaX zeolites are being characterized and the results are being correlated to DFT simulations (Groust et al. 2005).

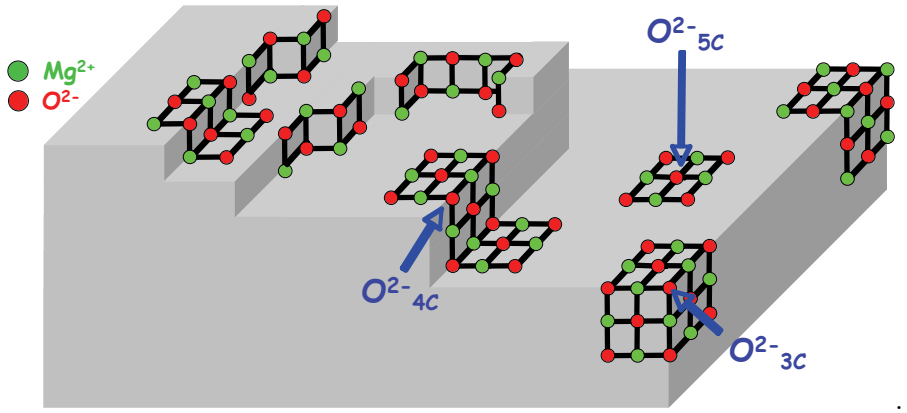

Figure D.51. Schematic illustration of the coordination of O_2- sites on an MgO surface.

Figure D.52 illustrates the *in situ* dispersive-EXAFS results acquired during the rehydration of Ni on NaX using the Soleil Synchrotron. Cobalt oxide nanoparticles are also being templated inside SBA-15 silicas. The resulting material contained 5 nm Co_3O_4 particles and was highly active for CO oxidation (Lopes et al. 2006; Lopes, Davidson, and Thomas 2007). Mesoporous materials are also being used as supports for hydrotreating catalysts. In the case of supported gold catalysts, the work involves the development of new methods for the synthesis of these catalysts with various oxide supports, and their application in reactions of selective hydrogenation and of oxidation for environmental purpose, such as the oxidation of carbon momoxide (Delannoy et al), the decomposition of volatile organic compounds (VOC), reduction of nitrogen oxides ($deNO_x$).

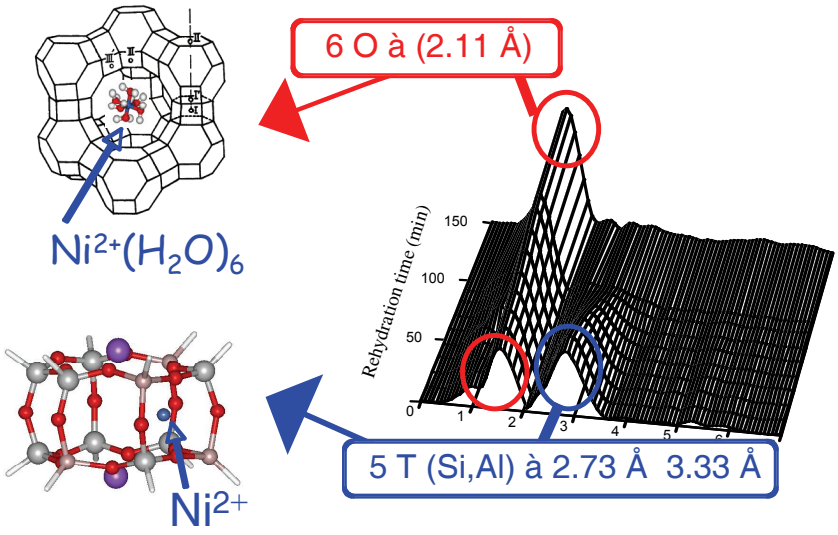

Figure D.52. Extended X-ray Absorption Fine Structure spectra acquired during the rehydration of a Ni/NaX catalyst (Groust et al. 2005).

Research in Group III (http://www.labos.upmc.fr/umr7609/pages/theme3.htm) focuses on understanding the catalytic properties of noble metals and nanostructured carbides at a molecular level. The carbides possess properties that resemble those of Pt-group metals and are being developed as potential replacements. Reactions of particular interest include catalytic reforming, CO and soot oxidation, NO_x SCR, isomerization, hydrotreatment and selective ring opening. The kinetics measurements are carried out at steady-state and under transient conditions in an attempt to isolate important reaction intermediates. The work involves significant international collaborations and has resulted in a significant number of publications and patents.

Research in Group IV is described at http://www.labos.upmc.fr/umr7609/pages/theme4.htm.

SUMMARY AND CONCLUSIONS

Catalysis is a priority area for France, and research at the LRS supports national initiative and is very well coordinated. Funding for research appears to be sufficient to support a large number of researchers and the necessary equipment and infrastructure. The results of research are disseminated via seminar, journal articles, monographs and patents. There is also a track regard of translation of the research findings into innovations as measured by the number of patents.

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Lopes, I., A. Davidson, and C. Thomas. 2007. Calibrated Co3O4 nanoparticles patterned in SBA-15 silicas: Accessibility and activity for CO oxidation. *Catalysis Comm*. 8(12):2105-2109.

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BACKGROUND

The Group of Inorganic Chemistry and Catalysis at the University of Utrecht's Debye Institute is headed by Professors Krijn de Jong and Bert Weckhuysen and comprised of 8 technical staff, 4 scientific staff including Associate Professor Frank de Groot and Assistant Professor Petra de Jongh, 10 postdoctoral fellows, 24 PhD students, and 5 Master's students. The group is a subset of the Department of Chemistry and belongs to the Faculty of Sciences of Utrecht University. Both homogeneous and heterogeneous catalysis have very well established histories and traditions at the University of Utrecht. The Inorganic Chemistry and Catalysis group has been a leading figure in the Netherlands as well as in the world in catalyst synthesis and characterization under working conditions. This has been the result of the significant advances made by Professors de Jong and Weckhuysen as well as by the previous directors, Professors Geus and Koningsberger. The Department of Chemistry as well as the governing board of Utrecht University view catalysis as an important enabling science and are therefore looking to expand the catalysis efforts in the near future.

The Inorganic Chemistry and Catalysis group at Utrecht University is closely integrated with other universities in the Netherlands as well as with industry to form a catalysis network. Professor Weckhuysen is currently the head of the Netherlands Institute for Catalysis Research (NIOK, http://www.niok.nl) which is a virtual institute for catalysis that is actively involved in research and education in catalysis across the Netherlands. It brings all of the Dutch universities in catalysis together with industry and with the government. This virtual institute is well coordinated, establishing very strong focused efforts of expertise across the country. Member universities work well together, respecting one another's' areas of expertise and playing off of each others' strengths to form an outstanding catalysis "team." Industry is directly integrated into the program and helps to provide a strong foundation in the short as well as in the long term. The Inorganic Chemistry and Catalysis group is an integral member of NIOK as it has strong expertise in the synthesis of nanomaterials and in the development and application of *in situ* spectroscopic methods that span the many length scales in heterogeneous catalysis, toward understanding catalytic performance. NIOK was recently awarded a €29 million center over 8 years in the area of biorenewables that has been named CATCHBIO (CATalysis for sustainable production of CHemicals from BIOmass; http://www.catchbio.com/). The consortium, directed by Professor Weckhuysen, will establish new catalytic materials and technologies to convert biomass fractions such as lignocellulose into renewable fuels, bulk chemicals, and pharmaceutical intermediates. The research will be carried out over various universities within NIOK and includes strong collaborative interactions with Shell, DSM, Sabic, Dow Chemicals, BASF, Albemarle Catalysts, Organon, VibSpec, and Hybrid Catalysis.

The Inorganic Chemistry and Catalysis group also actively participates in other national programs such as the National Research School Combination Catalysis (NRSCC) and European networks such as COST (European Cooperation in Scientific and Technical Research, http://www.cost.esf.org/) and Integrated Design of Catalytic Nanomaterials for Sustainable Production (IDECAT) (http://idecat.unime.it/).

RESEARCH AND DEVELOPMENT

The Inorganic Chemistry and Catalysis group is comprised of leading experts in the synthesis, *in situ* spectroscopic characterization, and performance of well-controlled heterogeneous catalytic materials. Its focus is on elucidating and exploiting the relationships between catalyst structure and function across a range of length scales from the atomic structure up through working reactor. The group is well integrated, with Professor de Jong leading focused efforts on catalyst synthesis and Professor Weckhuysen leading efforts on *in situ* characterization under working conditions. These areas were discussed with the WTEC team.

Nanostructured Materials for Catalysis and Hydrogen Storage

Professor de Jong described to WTEC panelists some of his efforts in the synthesis of: (1) nanostructured carbon materials for the use in the controlled dispersion of metals for hydrogenation, hydrotalcite, and nitrogen-containing carbon nanotubes as base catalysts and Mg and $NaAlH_4$ materials for hydrogen storage and (2) ordered mesoporous materials in order to directly control metal particle sizes together with pore size distribution such as Ni clusters in SBA-5 and supported Co particles for Fischer-Tropsch synthesis.

The group has synthesized well-controlled and well-ordered mesoporous silica and nanostructured carbon fiber substrates and have developed a suite of catalyst preparation methods, including chemical vapor deposition, adsorption and ion-exchange deposition and precipitation, and impregnation and drying in order to control the catalyst size, morphology, and interaction with the support. In particular, they have shown that deposition precipitation of active metal catalysts onto carbon supports can be used to achieve high catalyst loadings, very good dispersions, and high thermal stabilities. The carboxylic acid groups act as key anchoring sites. Professor de Jong and his group extended the approach to the nucleation of small basic metal oxide clusters as well. They have been able to successfully nucleate very small platelets or crystals of the basic hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}4H_2O$) materials onto carbon nanofibers in order to improve their mechanical stability and expose more of the edges (Winter et al. 2005; Winter, van Dillen, and de Jong 2005; and Winter et al. 2006). This led to significantly improved catalytic activity. The micrographs of the synthesized supported platelets on carbon nanofibers are shown in Figure D.53 A and B.

Their specific activity for acetone self-condensation was found to be significantly higher than that for the basic hydrotalcite material alone as is shown in Figure D.53 C. In addition, they were able to catalytically synthesize N-containing carbon nanotubes through the use of acetonitrile and pyridine precursors. These N-containing materials were used as base catalysts in the reaction of benzaldehyde and ethylcyanoacetate to form ethyl α-cyanocinnamate (van Dommele, de Jong, and Bitter 2006).

In their work on mesoporous silicas, they developed novel ways in which to ensure that the metal deposits within the pores of the support remain stable and do not sinter or agglomerate during calcinations or reduction (Sietsma et al. 2007). Current calcination methods, which use air, lead to significant degrees of particle agglomeration. Professor de Jong and his colleagues have developed a novel approach in which they use diluted NO rather than air to carry out the calcinations. This leads to little, if any, loss in dispersion, as shown in Figure D.54.

This approach has allowed the de Jong team to stabilize both Ni and Co in well-controlled mesoporous SBA-15. They demonstrated the unique use of electron tomography to examine the individual pores of NiO/SBA-15 and establish the particle size distributions and well as nearest and next-nearest neighbors. The results are shown in Figure D.55. In addition, it has allowed them to examine the stability of the particles and their dispersion over time. This provided a key link between structure and catalytic performance. In addition, they are developing novel software to obtain the data directly. In the past this was quite tedious and done by hand. They have now fully automated the image analysis process (Friedrich 2007).

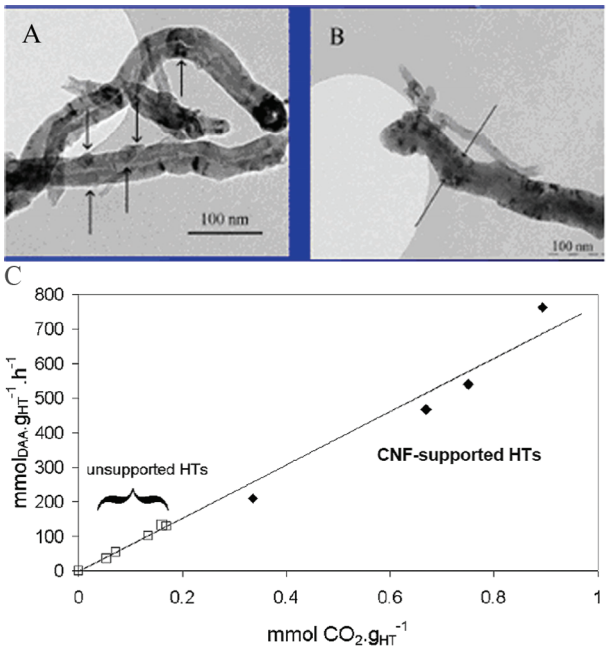

Figure D.53. Synthesis of hydrotalcite platelets onto carbon nanofibers. (*A & B*) TEM micrographs of 20 nm hydrotalcite platelets supported on carbon nanofibers. (*C*) Specific activity for acetone self-condensation (Winter et al. 2005; Winter, van Dillen, and de Jong 2005; Winter et al. 2006).

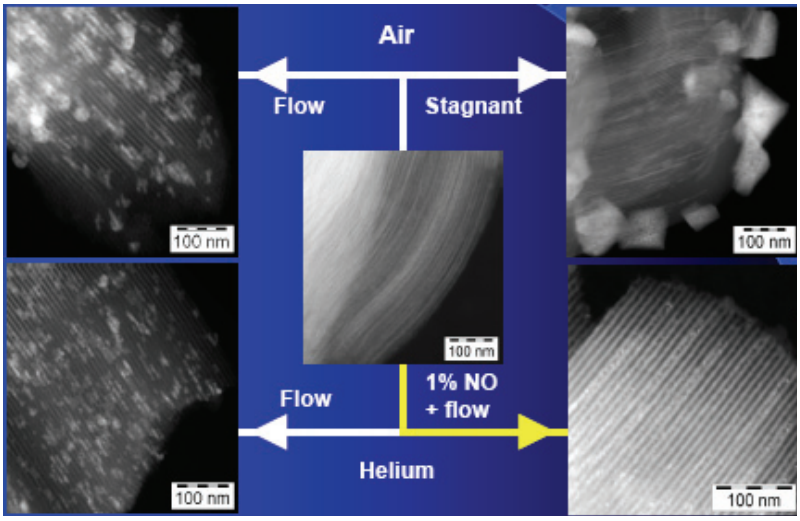

Figure D.54. Comparison of air and NO in both stagnant and flow systems for calcination of NiO/SBA-15. The novel use of NO in calcination helps to maintain metal dispersion and higher stability (Sietsma et al. 2007).

The synthesis of Co on well-controlled carbon nanofibers (CNF) and silica has allowed researchers in the de Jong group to answer a critical problem that has plagued our understanding of Fischer-Tropsch (FT) synthesis (Bezemer et al. 2005; Bezemer, Bitter, et al. 2006; Bezemer, Radstake, Koot, et al. 2006; Bezemer, Radstake, Falke, et al. 2006). For some time there has been some debate in the literature as to the nature of particle size effects on FT synthesis. The inability to measure and control metal particle size, however, has made it difficult to resolve this issue. The work by de Jong and colleagues provides a clear picture of the particle size effects, since they have demonstrated the ability to synthesize and control the particle size distributions of Co on both the CNF as well as on silica. Their results show that there is a minimum particle size of 6 nm whereby the activity drops off precipitously (see Figure 6.8).

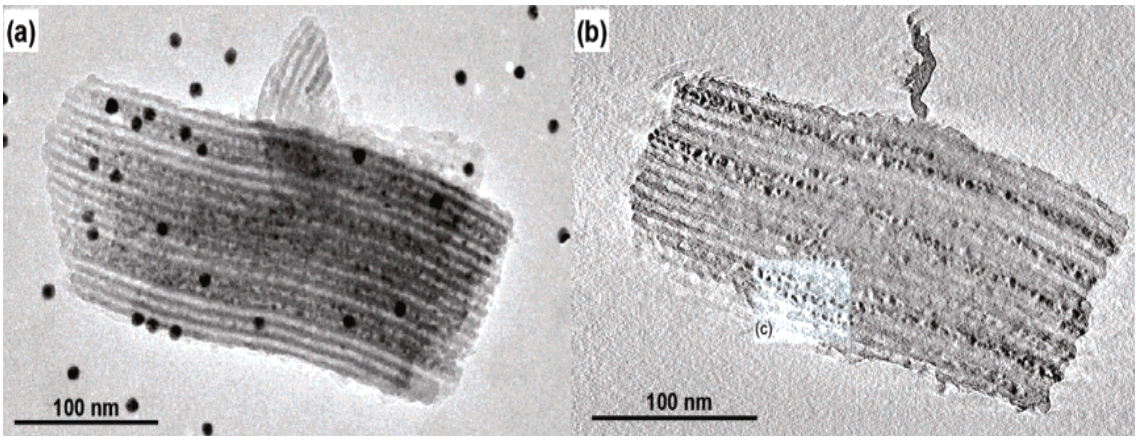

Figure D.55. The use of electron tomography to provide the resolution of individual pores of NiO/SBA-15. (a) conventional TEM image; (b) slice from tomogram.

The future efforts in this group are aimed at the precise preparation and characterization of nanoparticles in nanoporous materials though methods such as electron tomography. They hope to follow the genesis of nanoparticles of metal and metal oxides and to elucidate the influence of pore structure and size. They will exploit their understanding in order to aid in the immobilization of organicometallic groups to create multifunctional materials. In addition, they will examine the applications to biomass conversion and the synthesis of materials for hydrogen storage.

In Situ Characterization of Working Catalysts

Professor Weckhuysen discussed the recent efforts of his recent efforts in following heterogeneous catalysis under working conditions via integrated spectroscopic and microscopic characterization. The work is focused on "establishing the relationship between structure and function in heterogeneous catalysis at different length scales making use of spectroscopic methods" or "molecular heterogeneous catalysis as explored with *in situ* spectroscopy" (Weckhuysen 2002). They have made a number of significant advances in the field through the development and application of *in situ* spectroscopic methods and their application to understanding the active site and its environment under reaction conditions for hydrocarbon conversions (methane activation, propane dehydrogenation, propene oxidation); ethylene oligomerization/polymerization; environmental catalysis (catalytic decomposition of chlorinated hydrocarbons, automotive exhaust emissions), Fischer-Tropsch synthesis; and the valorization of renewables (conversion of glycerol, sucrose, and xylose). They are trying to establish a catalyst characterization "toolbox" by developing the protocols for combining a number of important *in situ* techniques to provide a more complete understanding of the working catalytic surface, including fluorescence, UV-Vis, EXAFS, XANES, EPR, NMR, Raman, and IR probes.

For example, through very clever engineering they have combined (XAFS, UV-Vis, and Raman) and (XAFS, SAXS, and WAXS) to establish novel *three-in-one* approaches to follow the changes in the surface chemistry as well as the properties of the catalyst. These approaches were used to follow the organic-inorganic interactions that lead to structure-directed synthesis of alumino-phosphate synthesis and the influence of metal ions. They demonstrated that both the template and the metal ions were important in directing the phase-selective synthesis and molecular control of these microporous alumino-phosphate systems. Time-resolved *in situ* Raman spectroscopy allowed them to follow the structural features of the synthesis gel and the influence of substituting in Zn^{2+} ions (Beale et al. 2006). Their results for the AlPO-5 materials indicated that the template conformation controlled the AlPO structure that formed. The synthesis of MeAPO-34, however, was governed by a complex interaction between the metal ion and the conformation of the organic template. The inorganic species resulted in true templating interactions, but this was controlled by the metal and its influence on positioning of the template. The template then acts as a structure-directing agent or as a space filler. Its specific role was difficult to determine. In a second study, they used the three-in-one SAX/WAX/XAFS setup to follow the formation of ZnAlPO-34 (Beale, van der Eerden, et al. 2006). They

demonstrated that the change in the conformer coincided with the formation of a prephase or the formation of microcrystals. There is a critical interaction between Zn^{2+} and the template that occurs when Zn is substituted into Al framework sites. This is necessary for the formation of the MeAPO-34 structure.

The group has also combined fluorescence microcopy and *in situ* UV-Vis microspectroscopy with catalytic activity tests to examine large 3D zeolite crystals in both the vapor and liquid phases in order to establish the accessibility of and reactivity of these crystals (Kox et al. 2007; Stavitski et al. 2007, Karwacki et al. 2007). They elegantly followed the styrene polymerization reaction, which allowed them to visualize shape selectivity in micropore channels down to the molecular level. Three-dimensional confocal fluorescence microscopy was used to follow the three-dimensional product distribution along the three-dimensional zeolite crystal.

The Weckhuysen group was the first to show how synchrotron tomographic energy-dispersive diffraction imaging (TEDDI) could be used in a noninvasive manner to provide time- and space-resolved information on the active catalytic component distribution as a function of the chemical and physical processes that occur during catalyst synthesis (Beale, Jacques, et al. 2007). TEDDI was used to determine the elemental as well as crystalline phase distributions over multiple dimensions to provide critical information on the physical and chemical processes that occur during catalytic impregnation as well as synthesis. The approach was used to map out 3D-type elemental and phase distribution information for Co/Al_2O_3 and Mo/Al_2O_3 hydrodesulfurization catalysts and show that the space- and time-resolved spectroscopic information typically gathered can oversimplify the relationship between catalyst preparation and performance. The results for the distribution of Mo and Co-Mo phases supported on Al_2O_3 are shown in Figure D.56. A similar approach can be followed by using the Magnetic Resonance Imaging technique (Bergwerff et al. 2007).

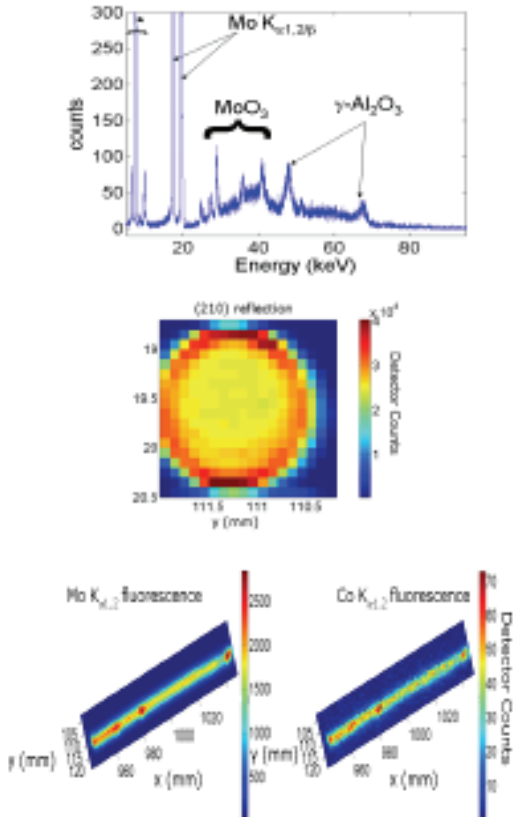

Figure D.56. Tomographic energy-dispersive diffraction image for Mo/Al_2O_3: (*top*) the detector signal, (*middle*) a y-z diffraction map from the signal, and (*bottom*) fluorescence maps of the concentration in a cylindrical plane of $Co\text{-}Mo/Al_2O_3$ catalyst.

In very recent efforts, researchers in this group have shown how *in situ* spectroscopic methods can be used to not only monitor the working state of the catalyst but also act to control its activity and stability (Bennici et al., 2007). They have established an expert-system control process based on monitoring the *in situ* Raman and UV-Vis spectra in a fixed bed catalytic reactor system, as is shown in Figure 3.4.

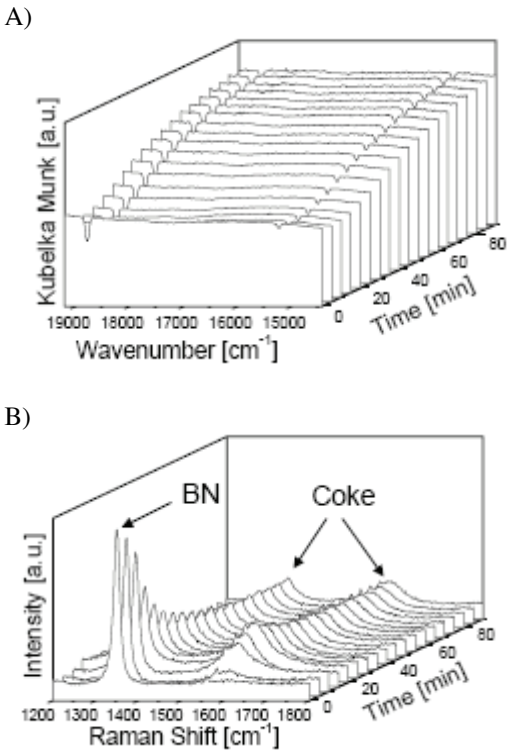

Figure D.57. Realtime (A) UV-Vis and (B) Raman spectroscopic monitoring of coke over a Cr/Al_2O_3 catalyst during propane dehydrogenation (Bennici 2007).

The approach was used to monitor the coking and deactivation of two different catalytic systems. The first involved a process for propane dehydrogenation over Cr/Al_2O_3 similar to that used in the Catofin process. Chromium here is reduced under reaction conditions as the result of coking. The coke must then be burned off in order to reoxidize the catalyst. Ultimately, the catalyst undergoes significant deactivation. Weckhuysen and colleagues demonstrated that *in situ* Raman and UV-Vis spectroscopic measurements could be used to directly follow the intensity of a band indicative of adsorbed coke that shows up at 1580 cm^{-1} in Raman as a function of processing. The characteristic Raman peaks could be used in a quantitative manner by using UV-Vis spectroscopy (Figure D.57 A and B).

These *in situ* spectroscopic measurements provide direct evidence of the amount of coke and the oxidation state of the catalyst together with the catalytic performance. As such they proved the baseline for online control, which was used to monitor the reduction and regeneration cycles.

This is shown in Figure D.58, where the activity is directly related to the coke levels. Higher coke levels lead to a loss in catalytic activity. The results interestingly show that some level of coking actually enhances catalytic performance. The reactor was controlled online by monitoring the level of coke. When the level of coke exceeded the set point value, as shown in Figure D.58, air was added automatically to the system to regenerate the catalyst.

The regeneration cycle was subsequently turned off when the amount of coke was reduced below a particular level. This level of monitoring and control was used to stage the levels of regeneration in order to help control catalytic activity, as in the cyclic reduction/regeneration cycles shown in Figure D.58. In addition to the work on Cr/Al_2O_3, this approach was used to monitor and control the oxidation of butane over VPO (vanadium phosphorus oxide). This work is quite unique in that it was the first to demonstrate that *in situ* spectroscopic monitoring could be used not only to follow but also to control a working catalytic system. The approach has received strong interest from industry, and the group is currently being funded by two major chemical companies in order to explore this approach to monitor and control catalytic systems at the pilot plant scale.

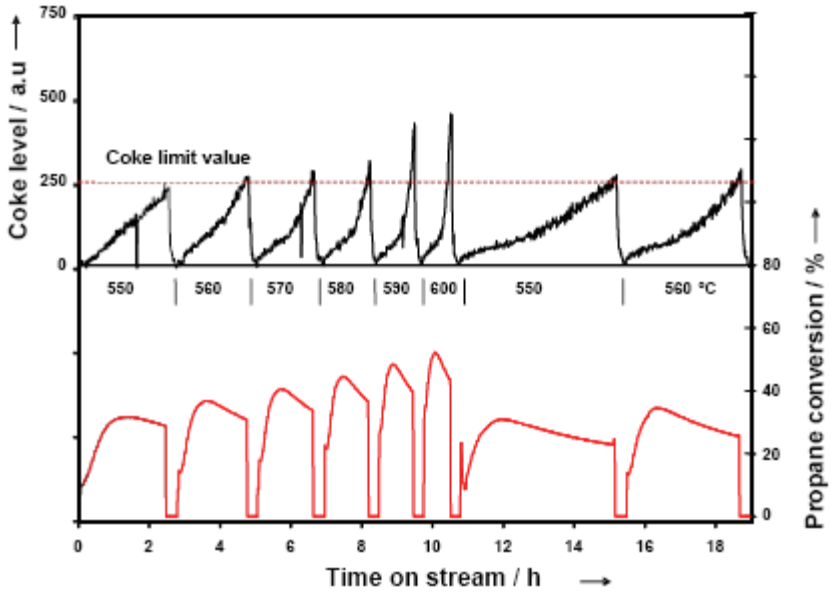

Figure D.58. Realtime monitoring and control of a propane dehydrogenation fixed bed reactor using *in situ* Raman and UV-Vis spectroscopy (Bennici 2007).

SUMMARY AND CONCLUSIONS

The Inorganic Chemistry and Catalysis group at the University of Utrecht's Debye Institute has a strong history in the synthesis of novel catalytic materials and their characterization. The current directors bring together outstanding expertise in the assembly of microporous, mesoporous, and nanosized materials; structural and surface chemistry; solid-gas and solid-liquid interactions; structure-activity relationships; and expert systems in heterogeneous catalysis, supramolecular, and environmental catalysis. They are playing leading roles in NIOK, NRSCC, and other European catalysis networks, as well as in international efforts. In addition, they have developed significant collaborations with industry. They are well recognized within the Utrecht University as well as in the international catalysis community for their pioneering contributions to the synthesis and *in situ* characterization of catalytic materials and their performance. As a result, their leadership is likely to continue and to grow.

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APPENDIX E. GLOSSARY

^{1}H NMR	Proton nuclear magnetic resonance
ADF	Annular dark-field
AES	Auger electron spectroscopy
AFM	Atomic force microscope
AIST	National Institute of Advanced Industrial Science and Technology (Japan)
ATR-IR	Attenuated total reflectance infrared (spectroscopy)
Au	Gold (chemical symbol)
BCC	Biomass catalytic cracking
BESSY (II)	Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (3rd-generation synchrotron radiation facility)
BET	Brunauer–Emmett–Teller surface area characterization/structure analysis method
BK21	Brain Korea 21st Century program
BN	Boron nitride
BOE	Barrels of oil equivalent
BSC-CNS	Barcelona Supercomputing Center – Centro Nacional de Supercomputación (the National Supercomputing Facility and National Supercomputing Center of Spain)
CAS	Chinese Academy of Sciences
CESCA	Centre de Supercomputació de Catalunya (Spain)
CESGA	Centro de Supercomputación de Galicia (Spain)
CNF	Carbon nanofiber(s)
CNR	Consiglio Nazionale delle Ricerche (National Research Council of Italy)
CNRS	Centre National de la Recherche Scientifique (National Center for Scientific Research, under the Ministry of Research, France)
CNTs	Carbon nanotubes
CO	Carbon monoxide (chemical symbol)
CPU	Central processing unit (computer)
CREST	Core Research for Evolutional Science and Technology (Japan Science and Technology Agency and the Research Development Corporation of Japan)
Cs	Cesium (chemical symbol)
CSIC	Consejo Superior de Investigaciones Cientificas (Council for Scientific Research, Spain)
CTI	Centro Técnico de Informática (Spain)
CUPS	KAIST's Center for Ultra-microchemical Process Systems
CVD	Chemical vapor deposition
DABCO	Diazabicyclo (2,2) octane
DCC	Deep catalytic cracking
DEFC	Direct ethanol fuel cell
DEMS	Differential electrochemical mass spectrometry

DFT	Density functional theory
DFTB	Density functional tight-binding
DICP	Dalian Institute of Chemical Physics, Chinese Academy of Sciences
DME	Dimethyl ether, a new fuel with properties similar to LPG (liquefied petroleum gas, propane gas), expected to replace diesel fuel and LPG
DMFC	Direct methanol fuel cell
DRIFTS	Diffuse reflectance infrared Fourier transform spectroscopy
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetry
DTU	Technical University of Denmark
EAC	Structure and Activity of Catalysts Group at the Institute of Catalysis and Petrochemistry (Spain)
EB	Ethylbenzene
EDS	Energy dispersive spectroscopy
EDX	Energy dispersive X-ray (micro)analysis/spectroscopy
ee	Enantiomeric excess
EELS	Electron energy-loss spectroscopy
ELCASS	European Laboratory (Consortium) of Catalysis and Surface Science
EMR	Electron magnetic resonance
EPR	Electron paramagnetic resonance, also known as electron spin resonance (ESR)
EPSRC	Engineering and Physical Sciences Research Council (UK)
ESEM	Environmental scanning electron microscope/y
ESR	Equivalent series resistance/resistant (measurement, calculation); electron spin resonance
ESRF	European Synchrotron Radiation Facility (Grenoble, France)
ETEM	Environmental transmission electron microscopy
EtOH	Ethanol
EUBIA	European Biomass Industry Association
EXAFS	Extended X-ray absorption fine structure
EXPEEM	Energy-filtered X-ray photoemission electron microscopy
FCC	Fluid catalytic cracking
fcc	Face centered cubic (structure)
FEG	Field-emission gun
FEI	FEI Company (multinational/German)
FESEM	Field-emission SEM
FHI	Fritz Haber Institute (Germany)
FIB	Focused ion beam
FID	Flame ionization detection
FP	Flame pyrolysis

FTIR	Fourier transform infrared (spectroscopy)
FTS	Fischer-Tropsch synthesis
GC	Gas chromatography
GIF	Gatan imaging filter
GTL	Gas to liquid
HAADF	High-angle annular dark-field
hcp	Hexagonal closest packing (structure)
HDM	Hydrodemetallization
HDO	Hydrodeoxygenation
HDS	Hydrodesulfurization
HMS	Hexagonal mesoporous silica
HPA	Heteropolyanions
HPLC	High-pressure liquid chromatography; high-performance liquid chromatography
HP-RAIRS	High-pressure reflection-absorption infrared spectroscopy
HREELS	High-resolution EELS
HREM	High-resolution electron microscopy
HRTEM	High-resolution transmission electron microscopy
ICP	Institute of Catalysis and Petrochemistry (Spain)
IDECAT	Integrated Design of Catalytic Nanomaterials for Sustainable Production (EU)
INSTM	Interuniversity Consortium on Science and Technology of Materials (Italy)
IP	Intellectual property
IR	Infrared
ISS	Ion scattering spectroscopy
ITQ	Instituto de Tecnología Química (Spain)
JSPS	Japan Society for the Promotion of Science
JST	Japan Science and Technology Agency
KAIST	Korea Advanced Institute of Science and Technology
KEK-PF	High Energy Accelerator Research Organization of Japan, Photon Factory
LEED	low energy electron diffraction
LEEM	Low-energy electron microscopy
LEIS	Low-energy ion scattering
LISF	Laser-induced surface fluorescence spectroscopy
LT-STM	Low-temperature scanning tunneling microscopy
MAS	Magic angle spinning
MCH	Methylcyclohexane
MeOH	Methanol
MEXT	Ministry of Education, Culture, Sports, Science and Technology (Japan)
MITI	Ministry of International Trade and Industry (Japan)

MRI	Magnetic resonance imaging
MS	Mass spectrometry
MTG	Methane to gasoline
MTO	Methanol to olefins
MWW	A type of zeolite structure
NEDO	New Energy and Industrial Technology Development Organization (Japan)
NEMAS	NanoEngineering Materials and Surfaces Center of the Politecnico di Milano (Italy)
NER	Nanoscale Exploratory Research programs of NSF
NEXAFS	Near-edge X-ray absorption fine structure
NIOK	Netherlands Institute for Catalysis Research
NIR	Near infrared
NIRT	Nanoscale Interdisciplinary Research Teams programs of NSF
NMR	Nuclear magnetic resonance
NoE	European Network of Excellence
NRSCC	National Research School of Combination Catalysis (The Netherlands)
NSF	National Science Foundation (U.S.)
ODH	Oxidative dehydrogenation reactions
OIM	Orientation image microscopy
OSC	Oxygen storage capacity
PAH	Polycyclic aromatic hydrocarbon
PDADMAC	Polydiallyldimethylammonium chloride
PED	Photoelectron diffraction
PEEM	Photoemission electron microscopy
PEM	Polymer electrolyte membrane (fuel cell)
PI	Principal investigator
PIRE	Partnership for International Research and Education program of NSF
PM	Particulate matter
PM-IRRAS	Polarization modulation-infrared reflection-absorption spectroscopy
PMO	Periodic mesoporous organosilica
PO	Propylene oxide
PrOx	Preferential oxidation (also PROX)
PSOFC	Pressurized solid oxide fuel cell
PTRF or PTRF-EXAFS	Polarization-dependent total-reflection fluorescence EXAFS
PVP	Poly(N-vinylpyrrolidone)
QEXAFS	Quick extended X-ray absorption fine structure
QM/MM	Quantum mechanical/molecular mechanical
QMS	Quadrupole mass spectrometer

QXAFS	Quick X-ray absorption fine structure
RAIRS	Reflection-absorption infrared spectroscopy
RC	Relative commitment of a country (to catalysis research measured in the bibliometric study, Appendix B)
RMB	Ren min bi, national currency of China
SAXS	Small-angle X-ray scattering
SBA-15	Mesoporous silica
SCAC	Single-crystal adsorption calorimetry
SCR	Selective catalytic reduction
SEM	Scanning electron microscopy/microscope
SFG	Sum frequency generation
SIMS	Secondary ion mass spectrometry (also, dynamic SIMS)
SKLC	State Key Laboratories of Catalysis (DICP, China)
SKLMRD	State Key Laboratory of Molecular Reaction Dynamics (DICP, China)
SMART	Ultrahigh-resolution spectromicroscope (SpectroMicroscope for All Relevant Techniques) (FHI, for use in BESSY)
SOFC	Solid oxide fuel cell
SPring-8	Large 3rd-generation synchrotron radiation facility, Harima Science Garden City Hyogo, Japan, of the Japan Synchrotron Radiation Research Institute (JASRI)
SSNMR	Solid-state NMR spectroscopy
STEM	Scanning transmission electron microscopy/microscope
STM/STS	Scanning tunneling microscopy/spectroscopy
SWCNT	Single-walled carbon nanotubes
syngas	Synthesis gas, a gas mixture that contains varying amounts of carbon monoxide and hydrogen generated by the gasification of a carbon-containing fuel to a gaseous product with a heating value
TAP	Temporal analysis of products
TBP	Tributylphosphine
TBPP	Tetra-3,5-di-ter-butyl-phenyl porphyrin
TDS	Thermal desorption spectroscopy
TEAOH	Tetraethylammonium hydroxide
TEDDI	Tomographic energy dispersive diffraction imaging
TEM	Transmission electron microscopy/microscope
TGA	Thermogravimetric analysis
TGA-DTA	Thermal gravimetric (or thermogravimetric) analysis – differential thermal analysis
TMCH	3,3,5 trimethyl cyclohexanone
tmeda	Tetramethylethylenediamine(also TMEDA)
TMP	Trimethylpentane isomers
TNT	Titania nanostructured thin films

TOF	Turnover frequency/ies
TPD	Temperature-programmed desorption
TPR/TPO	Temperature-programmed reduction/oxidation
TWC	Three-way catalysts or three-way catalytic converter for auto exhaust
UHV	Ultrahigh-vacuum
UHV-RAIRS	Ultrahigh vacuum reflection-absorption infrared spectroscopy
ULSD	Ultra-low-sulfur diesel
UPS	Ultraviolet photoelectron spectroscopy
USY	Ultrastable Y (zeolite)
UV	Ultraviolet
UV/Vis	Ultraviolet-visible (spectroscopy or spectrophotometry)
vis	Visible (spectrum, spectroscopy)
VOC	Volatile organic compound
VPO	Vanadium phosphorus oxide
VUV	Vacuum Ultraviolet
WAXS	Wide-angle X-ray scattering
WC	Tungsten carbide
WDS	Wavelength-dispersive spectrometer/try
WGS	Water gas shift (reactor, catalyst, etc.)
WHSV	Weight hourly space velocity
XAFS	X-ray absorption fine structure
XANAM	X-ray-aided non-contact atomic force microscopy
XANES	X-ray absorption near-edge structure
XAS	X-ray absorption spectroscopy
Xe	Xenon (chemical symbol)
XEDS	X-ray energy dispersive spectroscopy
XPEEM	X-ray photoemission electron microscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZP	Zeolite precursors

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