

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE May 1998	3. REPORT TYPE AND DATES COVERED Final Report 1993-96		
4. TITLE AND SUBTITLE Nanoscale Metal Oxide Particles as New Materials for the Destructive Adsorption of Toxic Chemicals			5. FUNDING NUMBERS DAAH04-94-G-0328	
6. AUTHOR(S) Kenneth J. Klabunde			8. PERFORMING ORGANIZATION REPORT NUMBER	
7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES) Department of Chemistry Kansas State University Manhattan, KS 66506			10. SPONSORING / MONITORING AGENCY REPORT NUMBER ARO 31049.25-CH	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.	
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.				
13. ABSTRACT (Maximum 200 words) Our interest has been in exploring and exploiting the enhanced surface chemical reactivates and huge surface areas of nanoparticles. This has led to the development of metal oxide nanoparticles as solid reagents that adsorb and simultaneously destroy toxic substances. The capacities of these destructive absorbents are high, and generally the toxic substance is "mineralized" by extraction of the heteroatom (P, Cl, Br, N, S) and conversion to a innocuous metal salt; volatile organics are released as relatively non-toxic hydrocarbons or carbon oxides which could be used as a fuel source.				
14. SUBJECT TERMS Metal Oxide, Nanoparticles, Adsorption, Detoxification			15. NUMBER OF PAGES 14	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

NANOSCALE METAL OXIDE PARTICLES AS NEW MATERIALS FOR THE
DESTRUCTIVE ADSORPTION OF TOXIC CHEMICALS

FINAL REPORT

MAY 1998

U.S. ARMY RESEARCH OFFICE

DAAHO4-93-6-0328

KANSAS STATE UNIVERSITY

APPROVED FOR PUBLIC RELEASE:
DISTRIBUTION UNLIMITED

THE VIEWS, OPINIONS, AND/OR FINDINGS CONTAINED IN THIS REPORT ARE
THOSE OF THE AUTHOR(S) AND SHOULD NOT BE CONSTRUED AS AN
OFFICIAL DEPARTMENT OF THE ARMY POSITION, POLICY, OR DECISION,
UNLESS SO DESIGNATED BY OTHER DOCUMENTATION.

Outline

I. Introduction

II. Review of Previous Work and Abstracts of Papers

- A. Second Generation Destructive Adsorbents
- B. Preliminary Scale-Up Experiments
- C. Surface Chemistry of Nanoscale Particles
- D. New Directions
- E. Reviews Written

I. Introduction

In the nanoscale regime neither quantum chemistry nor classical laws of physics hold. In materials (metals, semiconductors, or insulators) where strong chemical bonding is present, delocalization of valence electrons can be extensive, and the extent of delocalization can vary with size. This effect, coupled with structural changes with size variation, can lead to different chemical and physical properties depending on size. Indeed, it has now been demonstrated that a host of properties depend on the size of such nanoscale particles, including magnetic, optical, melting points, specific heats, and surface reactivity. Furthermore, when such ultrafine particles are consolidated into macroscale solids, these bulk materials sometimes exhibit new properties, for example, enhanced plasticity.

Our interest has been in exploring and exploiting the enhanced surface chemical reactivities and huge surface areas of nanoparticles. This has led to the development of metal oxide nanoparticles as solid reagents that adsorb and simultaneously destroy toxic substances. The capacities of these destructive adsorbents are high, and generally the toxic substance is "mineralized" by extraction of the heteroatom (P, Cl, Br, N, S) and

conversion to a innocuous metal salt; volatile organics are released as relatively non-toxic hydrocarbons or carbon oxides which could be used as a fuel source.

Extensions into the study of small metal particles has led to interesting surface chemistry and possible applications. Herein we have been concerned with metal-chlorocarbon reactions in water media.

From these points of view, we believe continued work on the chemistry of ultrasmall metal and metal oxide particles has importance both to basic and applied science. Further understanding of their synthesis, morphology, surface chemistry and their development into useful new materials is the driving force behind the prior work described herein.

II. Review of Previous Work and Abstracts of Papers

A. Second Generation Destructive Adsorbents

Abstracts of papers published, submitted, or in preparation are shown below:

Overlayer of Iron Oxide on Nanoscale Magnesium Oxide Crystallites

K.J. Klabunde, Abbas Khaleel, and Dong Park, High Temp. and Mater. Sci. **1995**, 33, 99-106 (invited paper in honor of John L. Margrave 70th birthday).

An overlayer of Fe_2O_3 on nanoscale MgO crystallites was prepared by adsorption of $\text{Fe}(\text{acac})_3$ followed by heat treatment. This $[\text{Fe}_2\text{O}_3]\text{MgO}$ composite served as a high-capacity reagent for reaction/decomposition of CCl_4 to form $[\text{Fe}_2\text{O}_3]\text{MgCl}_2$ plus CO_2 . The Fe_2O_3 overlayer served as a catalyst for efficient $\text{Cl}^-/\text{O}^{2-}$ ion exchange with the inner layers of MgO . The $[\text{Fe}_2\text{O}_3]\text{MgO}$ high surface area composite is a promising reagent for the one-step decomposition/ mineralization of chlorocarbon and chlorofluorocarbons at temperatures near 400°C .

Iron Oxide and Magnesium Oxide Support as a New Destructive Absorbent for Chlorinated Hydrocarbons

A.Khaleel and K.J. Klabunde, Nanophase Materials, G.C. Hadjipanayis and R.W. Siegel, editors, Kluwer Academic Publishers, Netherlands, 1994, 785-788.

In this study an overlayer structure of iron oxide on magnesium oxide support and pure magnesium oxide was synthesized in ultra fine particles of high surface area. The surface structure of Fe/MgO particles was studied by XPS, Mössbauer and XRD spectroscopy and surface chemisorption of CO₂. The potential of both compounds to react with and decompose CCl₄ was studied. Infrared (IR), powder X-Ray Diffraction (XRD) and GAS Chromatography (GC) study prove that magnesia-supported iron oxide (Fe/MgO) is about 15 times more efficient in reacting with and decomposing CCl₄ than pure MgO.

**Nanoscale Metal Oxides as Destructive Adsorbents.
New Surface Chemistry and Environmental Applications**

K.J. Klabunde, D.G. Park, J.V. Stark, O. Koper, S.Decker, Y. Jiang, and I. Lagadic, Fine Particle Technology: From Micro to Nanoparticles, E. Pelezzetti, editor, Kluwer Academic Publishers, NATO ASI Ser., Ser. 3, 12, 691-706 (1996).

An aerogel procedure combined with hypercritical drying has yielded magnesium oxide and calcium oxide in ultrafine surface area forms. These nanoparticles of MgO and CaO possess intrinsically higher surface reactivities, and serve as destructive adsorbents for a variety of toxic substances, including organophosphorus compounds, and chlorocarbons. They also serve to adsorb large amounts of gases very strongly, such as CO₂, SO₂, SO₃, and HX. A second generation of even more effective destructive adsorbents has been prepared by depositing a monolayer of transition metal oxide on the MgO or CaO nanoparticles, for example [Fe₂O₃]MgO, [NiO]CaO, [ZnO]MgO, and others. As a test reaction, CCl₄ + [Fe₂O₃]MgO → [FeCl_x]MgCl₂ + CO₂ was employed. This gas-solid reaction was facilitated and enhanced by two things: (1) Unusual morphology of nanoscale MgO, probably because of exposure of {111} crystal faces and high concentrations of edge sites and defect sites, and (2) the presence of the thin layer of Fe₂O₃ (or other transition metal oxide), which allows a catalytic O²⁻/Cl⁻ solid state ion/ion exchange to take place. The reaction proceeded to almost stoichiometric proportions when Fe₂O₃ was present, which indicates that the surface Fe₂O₃ - FeCl_x layer is mobile and dynamic, allowing continual O²⁻/Cl⁻ exchange deeper into the nanoparticle. Morphological studies were aided by Atomic Force Microscopy experiments, which will also be discussed.

**Iron Oxide Magnesium Oxide Composites and Method for Destructive of
Chlorinated Hydrocarbons Using Such Composites**

K.J. Klabunde, A. Khaleel, U.S. Patent 5,712,219 S/N 224, 705, Filed 4/8/94; Docket Number 22908, January 27, 1998.

C. Moh, Y. Jiang, S. Decker, K.J Klabunde, work in progress

A series of $[M_xO_y]MgO$ and $[M_xO_y]CaO$ layered nanoparticles and microparticles have been prepared and tested for efficacy of destructive adsorption of CCl_4 . It has been found that $[Fe_2O_3]CP-MgO$ (where CP-MgO is conventionally prepared material) is about 60% as effective as $[Fe_2O_3]AP-MgO$ (where AP is aerogel prepared -- our smallest particles). Furthermore, comparisons of Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn oxides as shell materials have indicated that V_2O_5 , Mn_2O_3 , and Fe_2O_3 are most effective.

B. Preliminary Scale-Up Experiments

Shubham Mahashwari, K.J. Klabunde and W. Walawender

A chemical engineering student chose as a project the scale-up of destructive adsorption technology for the $CaO + CCl_4$ reaction.

A bench-scale reactor for use of destructive adsorbent on 100g scale has been designed and built. Preliminary experiments show that a fixed-bed reactor worked reasonably well for CP-CaO as weakly agglomerated particles. With $[Fe_2O_3]CP-CaO$ efficiency was improved, but bed morphology was a problem (melding of particles as reaction proceeded caused pressure increases).

C. Surface Chemistry of Nanoscale Particles

Destructive Adsorption of Chlorinated Hydrocarbons on Ultrafine (Nanoscale) Particles of Calcium Oxide

Olga Koper, Y-X Li, K.J, Klabunde, Chem. of Materials, **1993**, 5, 500-505.

Ultrafine particles of CaO react with CCl_4 to yield $CaCl_2$ and CO_2 . Phosgene is an intermediate product but can be avoided if excess CaO is employed. The reaction with $CHCl_3$ yields $CaCl_2$, CO and H_2O , while C_2Cl_4 yields $CaCl_2$ carbon, and $CaCO_3$. Thermodynamically these are all favorable reactions, but kinetic parameters demand that high surface area CaO be used. However, under the right conditions multiple layers of the CaO particles can be converted to $CaCl_2$. An aerogel/autoclave method for the preparation of high surface area CaO is described.

Heterophasic Isotope Exchange in Nanoscale Metal Oxide Particles. Lattice Oxygen and Surface OH Groups with Water Vapor (D_2O and $H_2^{18}O$)

Y.-X. Li and K.J. Klabunde, Chem. of Materials, **1992**, 4, 611-615.

Ionic solids MgO, CaO, and Fe_2O_3 exchange surface and lattice oxide anions with $H_2^{18}O$ as monitored by pulsed reactor-GC-MS studies. Depending on the temperature, the

process can be controlled to exchange only OH, or additional surface lattice O^{2-} , or additionally, interior lattice O^{2-} (up to 16 layers deep). Exchange of surface oxide has an activation energy 5 times lower than exchange of bulk-lattice oxide, and the latter is probably controlled by E_a (diffusion). High surface area, small particle size MgO samples exchange most readily. Exchange studies with D_2O have shown that surface OH can be quantitated by the same pulsed reaction-GC-MS technique. These experiments have allowed the synthesis of isotopically labeled $Mg^{18}O$, which has proven useful for clarifying surface adsorption/decomposition chemistry. An example is given where the $Mg^{18}O$ yielded labeled formic acid in the surface and lattice oxide can take part in such adsorption/decomposition processes.

Cluster Quantum Chemical Study of the Interaction of Dimethyl Methylphosphonate with Magnesium Oxide

N.U. Zhanpeisov, G.M. Zhidomirov, I.V. Yudanov and K.J. Klabunde,
J. Phys. Chem., **1994**, 98, 10032-10035

In the framework of a supermolecular approach using the MINDO/3 method, the various channels of Dimethyl Methylphosphonate (DMMP) adsorption on a magnesium oxide surface are considered. On a basis of calculation results the possible mechanism of destructive adsorption of DMMP on MgO is discussed.

Destructive Adoption of Chlorinated Benzenes of Ultrafine (Nanoscale) Particles of Magnesium Oxide and Calcium Oxide

Y.-X. Li and K.J. Klabunde, *Env. Sci. & Tech.*, **1994**, 28, 1248-1253.

The thermodynamically favored but kinetically inhibited exchange of oxide for chlorine in the reaction of MgO/CaO with chlorinated benzenes has been investigated. In order to enhance kinetic parameters, MgO/CaO particles with very large surface areas have been employed. The presence of MgO/CaO allows the destructive adsorption of chlorinated benzenes at lower temperatures than simple pyrolysis or combustion processes. The presence of hydrogen as a carrier gas allows still lower temperatures to be employed. Main reaction pathways have been deduced for mono-, di-, and trichlorobenzenes over MgO and CaO of varying surface areas and using helium, air, and hydrogen as flow gases. Significant differences between MgO and CaO have been realized, perhaps due to the fact the MgO can be prepared in higher surface areas. For example, CaO induces more carbon formation. A search for certain trace toxins as products (particularly the dibenzo-p-dioxin backbone with 0-3 chlorine substituents) was carried out. Under our analysis conditions, it was determined that such products were not formed under any circumstances with MgO, and if oxygen in the carrier gas was absent, no dioxins were formed with CaO either. However, with low surface area CaO and air as a flow gas, dibenzo-p-dioxin (no chlorine substituents) and a monochloro derivative were produced in small amounts.

Destructive Adsorption of Carbon Tetrachloride in Iron(III) Oxide

P.D. Hooker and K.J. Klabunde, Env, Sci. & Tech., **1994**, 28, 1243-1247

The reaction between α -Fe₂O₃ and CCl₄ has been studied in order to investigate the potential of iron oxide as a destructive reagent for chlorinated organic compounds. The reaction has been studied between 400 and 620° in a fixed-bed pulse reactor. The effect of temperature, the contact time of the pulse of CCl₄ with the α -Fe₂O₃, and the ratio of iron oxide to CCl₄ have been investigated. The products have been analyzed (CO₂, FeCl₂ + FeCl₃, Cl₂ and small amounts of C₂Cl₄ and graphite; COCl₂ is a short-lived intermediate), and a mechanism has been proposed for the decomposition of the CCl₄ over the oxide.

Comparison of Nanoscale Calcium Oxide Versus Commercial calcium Oxide with Respect to Decomposition of Carbon Tetrachloride

O. Koper and K. J. Klabunde, Nanophase Materials, **1994**, 789-792,
G.C. Hadjipanayis and R.W. Siegel, editors, Kluwer Academic Publishers, Netherlands.

The increasing amount of chlorocarbons in our environment causes a need to find an effective and inexpensive way for their destruction. Calcium oxide seems to be a good choice as the adsorbing and decomposing agent. Three different types of calcium oxide were studied to determine the amount of carbon tetrachloride that could be decomposed: commercial calcium oxide, conventionally prepared calcium oxide, and autoclave prepared calcium oxide. The amount of decomposed chlorocarbon was established using gas chromatography and the products were studied by gas chromatography-mass spectrometry. The dependence of the surface area on the decomposition was determined. We found that the best type of calcium oxide was autoclave prepared because it decomposed the most and the decomposition started at the lowest temperature, 350°C. Some fundamental studies connected with the comparison of conventionally and autoclave prepared calcium oxides are also discussed.

Destructive Adsorption of Chlorinated Benzene on Ultrafine (Nanoscale) Particles of Magnesium Oxide and Calcium Oxide

Y.-X. Li, H. Li and K.J. Klabunde, Nanophase Materials, **1994**, 793-796,
G.C. Hadjipanayis and R.W. Siegel, editors, Kluwer Academic Publishers, Netherlands.

The exchange of oxide for chloride in the reaction of MgO or CaO with chlorinated hydrocarbons has been investigated on a fully automatic reactor-GC-MS system. The presence of MgO or CaO allows destruction of chlorinated benzenes at lower temperatures than simple pyrolysis or combustion processes. The presence of hydrogen as a carrier gas allows still lower temperatures to be employed. Decomposition have been observed for mono-, di-, and tri-chlorobenzenes over MgO and CaO of varying

surface areas, and using helium air, and hydrogen as flow gases. CaO induces more coupling of arenes and more carbon formation compared with MgO. A careful search for true toxins as products (particularly dioxins) was carried out. With low surface area CaO and air as a flow gas, dioxin and monochlorodioxin were produced in a small amounts. However, nanoscale MgO did not allow formation of these toxic substances.

Decomposition of CCl_4 on CaO

O.B. Koper, E.A. Wovchko, J.A. Glass, Jr., J.T. Yates, and K.J. Klabunde
Langmuir, **1995**, 11, 2054-2059.

Transmission infrared spectroscopy was used to monitor $\text{CCl}_x(\text{a})$ intermediate surface species formed during the decomposition of CCl_4 on high surface area calcium oxide. Carbon tetrachloride was adsorbed on calcium oxide at 113 K. During CCl_4 desorption, additional infrared bands at 801, 787, 775, 765, and 751 cm^{-1} were observed in the temperature range 110-250 K. These bands, which disappeared in the temperature range 150-250 K, were attributed to the formation and depletion of $\text{CCl}_x(\text{a})$ species as C-Cl bonds are broken and Ca-Cl bonds are formed on the CaO surface. Carbon tetrachloride (^{13}C labeled) was employed to prove that the infrared bands of the surface intermediates were due to C-Cl vibrational modes. To compare carbon tetrachloride decomposition on different types of calcium oxides, both autoclave prepared (nanoscale particles) and conventionally prepared CaO were investigated.

Nanoscale Magnesium Oxide Used to Adsorb SO_2 and CO_2

J.V. Stark, K.J. Klabunde, Nanophase Materials, **1994**, 797-800, G.C. Hadjipanayis and R.W. Siegel, editors, Kluwer Academic Publishers, Netherlands.

Sol-gel techniques and heat treatments have been employed to prepare nanoscale, high surface area magnesium oxide with properties unique from its conventionally prepared counterpart. Surface area and reactivity are highly related to their thermal treatment. Reactivities of two magnesium oxides with respect to adsorption of sulfur dioxide and carbon dioxide will be demonstrated. Insight to the reactive surface sites on nanoscale magnesium oxide will be given.

Nanoscale Metal Particles as Chemical Reagents, Intrinsic Effects of Particle Size on Hydroxyl Content and on Reactivity and Acid/Base Properties of Ultrafine Magnesium Oxide

H. Itoh, S. Utamapanya, J.V. Stark, K.J. Klabunde and J.R. Schlup,
Chem. of Materials, **1993**, 5, 71-77.

Two sizes of ultrafine magnesium oxide particles have been carefully compared for intrinsic surface chemistry differences. Ultrahigh surface area MgO(400-650 m²/gm) prepared by an autoclave hypercritical drying (procedure has been compared with conventionally prepared MgO(100-300 m²/gm) for hydroxyl surface concentration (also residual OCH₃) pyridine, benzene, xylene, and nitrobenzene adsorption. The aerogel-prepared material exhibited the highest surface area (650 m²/g) after a 300°C heat treatment, while the conventional sample's surface area went up to 300 m²/g after a 400°C heat treatment. Both FT-IR/photoacoustic and conventional transmission IR spectroscopes were employed to monitor the adsorbed species. Amounts of materials adsorbed were also quantitatively determined. Careful comparison between the smaller and larger particle MgO were made. It was shown that surface -OH concentrations were similar but that the larger particles allowed more geminal pair reactions of -OH with AlEt₃ to yield EtAl-(O₂)(ad) rather than Et₂Al-O(ad). It was also found that the MgO particles adsorbed pyridine on the Mg²⁺ sites and not the Bronsted sites. However, benzene did adsorb on Bronsted sites, and IR shifts showed that the smaller particles exhibited weaker Bronsted acidity. Nitrobenzene adsorption suggested weaker Lewis basicity as well. It is proposed that basic/reducing character depends more on domains and is encouraged by larger particle size and Bronsted acidity is also encouraged by -OH surface island domains. Overall, the results show that particle size can have intrinsic effects on surface chemistry.

**Nanoscale Metal Oxide Particles/Clusters as Chemical Reagents
Adsorption of Hydrogen Halides, Nitric Oxide and Sulfur Trioxide on Magnesium
Oxide Nanocrystals and Compared with Microcrystals**

Jane V. Stark and Kenneth J. Klabunde, Chem. Mater., **8**, 1913-1918 (1996).

Adsorption of HCl, HBr, NO and SO₃ on nanoscale MgO(AP-MgO) and microscale MgO(CP-MgO) has been studied. The higher surface area of AP-MgO allows a higher capacity of these gases to be adsorbed/mol MgO. However, at pressures of 100 Torr or higher, the amount adsorbed/nm² for HX and SO₃ is larger on the microcrystals. This is explained as due to the formation of ordered multilayers of adsorbate on the more perfect crystals of CP-MgO (adsorption on flatter, more extended planes). In the case of NO, the different surface chemistry of AP-MgO vs. CP-MgO is again demonstrated. In this case, AP-MgO adsorbed more NO/nm² and NO₂, N₂, and N₂O were formed on the surface. The high surface area and unusual surface reactivity of nanoscale MgO allows it to be considered as a new type of adsorbent as well as a near surface stoichiometric chemical reagent.

**Nanoscale Metal Oxide Particles/Clusters as Chemical Reagents, Enhanced
Adsorption of Acid Gases and Pressure Dependence on Magnesium Oxide**

Jane V. Stark, Dong G. Park and Kenneth J. Klabunde, Chem. Mater., **8**, 1904-1912 (1996).

Surface adsorptive properties of nanoscale MgO particles have been compared with more conventional samples. Morphologically the nanoparticles (AP-MgO) are unique and very different from the conventional samples (CP-MgO), and AP-MgO possesses more defect, edge and corner sites, higher surface area and more higher index surfaces. The number of residual surface -OH groups/nm² is similar for both types of samples. Differences in adsorptivity of SO₂ and CO₂ at relatively low pressure (20 Torr) were determined by gravimetric means. Much larger quantities were adsorbed by AP-MgO. These results, coupled with FTIR studies, are rationalized as due to higher intrinsic surface reactivity coupled with higher concentrations of lower coordination ions on the nanoparticle. Pressure studies showed, however, that as 100 torr SO₂ or CO₂ was reached, the CP-MgO samples exhibited higher absorptive capacities. Quantitative determinations of SO₂(CO₂) loading support that this difference can be attributed to multilayer adsorption on CP-MgO, which with its flatter, extended planes can apparently form more ordered multilayer structures and thus physically adsorbed more SO₂ (or CO₂). This process of chemisorption was dynamic, and oxygen scrambling occurred when SO₂ and Mg¹⁸O nanoparticles were in contact. In the case of SO₃, large amounts of surface sulfates were detected by FTIR. Overall, our results indicate that nanoparticles of MgO possess unique surface chemistry and their high surface reactivity coupled with high surface area allowed them to approach the goal of being surface stoichiometric chemical reagents.

**Adsorption and Decomposition of Organophosphorus Compounds
on Nanoscale Metal Oxide Particles. In Situ GC-MS Studies of Pulsed
Microreactions over Magnesium Oxide**

Y.-X. Li, O. Koper, M. Atteya, and K.J. Klabunde, Chem. of Materials, **1992**, **4**, 323-330.

Using an in situ pulse reactor GC-MS system, the thermal decomposition of organophosphorus compounds (as models of nerve agents) has been compared with their destructive adsorption on high surface area magnesium oxide. Dramatically lower temperatures are required when MgO is present. Volatile products evolved were formic acid, water, alcohol and alkenes. At higher temperatures, CO, CH₄, and water predominated. Phosphorus residues remained completely immobilized. Addition of water enhanced the facility of MgO to destroy these compounds, and in fact, water pulses were found to partially regenerate a spent MgO bed. Using ¹⁸O labeling, some aspects of the reaction mechanism were clarified and in particular showed that oxygen scrambling occurred. Surface OH and MgO groups transferred oxygen in the formation of formic acid, and surface mobility and reactivity of adsorbed groups very high. The substantial capacity of high surface area MgO for destruction and immobilization of such toxic substances make it attractive for air purification schemes as well as solid reagents for destruction and immobilization of bulk quantities of hazardous phosphorus compounds or organohalides.

D. New Directions

Destruction of Organohalides in Water Using Metal Particles: Carbon Tetrachloride/Water Reactions with Magnesium, Tin, and Zinc

T. Boronia, K.J. Klabunde and G. Sergeev, Env. Sci & Tech., 1995, 29, 1511-1517

As a possible method for degrading chlorocarbons in contaminated water supplies, the reactions of metallic magnesium, tin, and zinc with $\text{CCl}_4/\text{H}_2\text{O}$ mixtures have been studied. In the case of Mg, oxidation by water overwhelmed the Mg- CCl_4 reaction. However, Sn and Zn were successfully used to degrade CCl_4 . Major products in the Sn/ $\text{CCl}_4/\text{H}_2\text{O}$ system were CO_2 , CHCl_3 , SnO_2 , and HCl with smaller amounts of CHCl_3 and CH_2Cl_2 . In the case of Zn/ $\text{CCl}_4/\text{H}_2\text{O}$, the major products were ZnCl_2 , $\text{Zn}(\text{OH})_2$, and CH_4 with CHCl_3 , CH_2Cl_2 and CH_3Cl as intermediate products. Thus, Sn and Zn behave quite differently with the final carbon-containing product, with Zn being CH_4 but with Sn being CO_2 . This is rationalized by the competing reactions of a possible intermediate Cl_3CMCl , which can be protonated by H_2O to give CHCl_3 or eliminate CCl_2 (which subsequently reacts with water to form CO_2 and HCl). Metal surface areas are also important, and the most active metal samples were prepared by a metal vapor-solvent codeposition were also effective, only with lower reaction rates.

Preparation of Small Particles of Titanium (IV) Oxide

C.R. Mohs and K.J. Klabunde, Nanophase Materials, 1994, 121-124,
G.C. Hadjipanayis and R.W. Siegel, editors, Kluwer Academic Publishers, Netherlands.

Preparation of small particles of Titanium (IV) oxide, TiO_2 , is important because understanding the particle size effects of TiO_2 in a photocatalytic system is beneficial. Titanium (IV) oxide was prepared by an aerogel technique, which was varied by preparing the gel in different solvents, namely, methanol, 1-butanol, and toluene. Using different solvents altered the size and surface area of the particles, which were characterized by powder X-ray Diffraction and Transmission Electron Microscopy.

Cathy Mohs and K.J. Klabunde

Continued work in TiO_2 , $[\text{TiO}_2]\text{MgO}$, and $[\text{Fe}_2\text{O}_3]\text{MgO}$ nanoparticles as photocatalysts for CHCl_3 degradation has shown that there is an optimum size; smaller is not necessarily better. Due to our relatively unspectacular results, and the mounting competition, we have terminated this project at least for now. However, we have sent some TiO_2 samples to Dr. R. Bowman for femtosecond spectroscopy studies of hole-pair lifetimes.

Eric Lucas and K.J. Klabunde

We are attempting to design "benign chemical synthesis" schemes based on our nanoparticles as chemical reagents. For example: $R_2CCl_2 + CaO(s) \rightarrow R_2C=O + CaCl_2$ is being investigated.

Nanjing Sun and K.J. Klabunde

Literature teaches that MgO-Na is a solid superbase and can carry out a variety of hydrocarbon transformations through carbanion type mechanisms. We are attempting to extend this to nanoparticles, where superbase sites may be generated, where each particle might contain high electron density trapped in a finite volume and at special surface sites.

Alexander Bedilo and K.J. Klabunde

Literature also teaches that ZrO_2-SO_4 is a solid superacid and can cause a variety of hydrocarbon transformations through carbo-cation mechanisms. We are attempting to extend this to nanoparticles, where superacid sites may be generated, and each particle may contain superacid sites trapped in a finite volume and as special surface sites.

E. Reviews Written

K.J. Klabunde and Cathy Mohs, "Nanoscale Particles and Nanostructural Materials", an invited review with 250 references that was published in a book series Materials Chemistry, L. Interrante and M. Hampden-Smith, VCH Pub., "Chemistry of Advanced Materials: An Overview.," L.V. Interrante, M.J. Hampden-Smith, editors, Wiley-VCH, Inc.,; 271-327 (1998).

Chemical Synthesis of Nanophase Materials

K.J. Klabunde, J.V. Stark, O. Koper, C. Mohs, A. Khaleel, G. Glavee, D. Zhang, C.M. Sorensen, G.C. Hadjipanayis, Nanophase Materials, 1994, 1-19, G.C. Hadjipanayis and R.W. Siegel, editors, Kluwer Academic Publishers, Netherlands.

A short review of important methods for the chemical synthesis of nanoscale particles is presented: transition metal ion reduction by sodium borohydride in aqueous and nonaqueous solvents, nonaqueous reduction using alkali metals, precipitation of metal ions by hydroxide ion, aerogel synthesis, reverse micelle techniques, gas phase aerosol methods, and metal vapor deposition. Nucleation in cold matrices is discussed. Emphasis is placed in chemical reaction stoichiometries, reaction conditions, and isolation techniques. The uses of

nanophase materials as novel reagents is considered along with their unusual physical properties.

Catalysis and Surface Chemistry: Metal Clusters/Nanoscale Particles

K.J. Klabunde, Y.-X. Li and K.J. Klabunde, Nanophase Materials, 1994, 757-769, G.C. Hadjipanayis and R.W. Siegel, editors, Kluwer Academic Publishers, Netherlands.

Recent examinations have shed light on how metal clusters behave as catalysts. Especially by studying bimetallic systems, electronic and ensemble (geometric) effects have been clarified. Strong metal support interactions (SMSI) may be explained due to "decoration effects". It is apparent that morphology of the particles is extremely important in determining catalytic properties. Recent experiments in metal vapor chemistry for producing various catalytic morphologies are discussed, with special emphasis on the Pt⁰-Sn⁰ system. Finally, new studies of gas phase metal cluster-hydrocarbon reactions are briefly reviewed with emphasis on Pt(n) and Nb(n).

Students, Postdoctorals, and Research Associates Involved in this Research Over Past Five Years

- | | |
|---------------------|---|
| Jane Stark | M.S. in 1995; "Characterization and Studies of Reactivity of Magnesium Oxide" teaching high school in Houston |
| Olga Koper | Ph. D. in 1996; "Properties of High Surface Area Calcium Oxide and Its Reactivity Towards Chlorocarbons" |
| Cathy (Rogers) Mohs | Ph.D. in 1996; "Nanoscale Particles of MgO and [Fe ₂ O ₃]MgO as Destructive Adsorbents and TiO ₂ as a Photocatalyst for Environmentally Hazardous Materials," |
| Abbas Khaleel | M.S. in 1993; "Iron Oxide on Magnesium Oxide Support as a New Destructive Adsorbent for Chlorinated Hydrocarbons," has finished a Ph.D. degree in a related field and is doing postdoc work. |
| Yong-Xi Li | former postdoc: now manager of an analytical lab in Ohio |
| Paul Hooker | former postdoc; now Assistant Prof. at Salt Lake City Comm. College |
| Hidenobu Itoh | former visiting Prof.; now Professor at Kitami Inst. Hokkaido, Japan |

- Alexander Bedilo postdoc; has returned to Boriskov Catalysis Institute in
Novosibirsk, Russia
- Tatiana Boronia postdoc; has returned to Moscow State University, Russia
- Shawn Decker current Ph.D. student
- Yan Jiang M.S. in 1996; "Destructive Adsorption of Chlorinated Compounds
on Transition Metal Oxide Created Magnesium Oxide,"
now working for an instrument company in New Jersey.
- Shabhum Mahashwari M.S. Chem. Eng. in 1996; "Bench Scale Process
Development Studies for Destructive Adsorption of
Chlorocarbons," now studying for an MBA.
- Erik Lucus current Ph.D. student
- Alanna Li M.S. in 1997; "Reductive Degradation of Chlorinated Ethylenes by
Zero-Valent Zn in Aqueous Solutions," now working on
Ph.D. degree.
- Nainjing Sun current Ph.D. student