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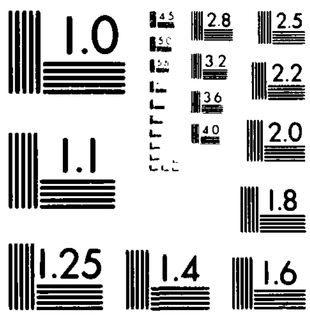

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Fundamental Studies of the Structure and Chemistry of Solid Surfaces

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FINAL REPORT

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AFOSR-80-0103

1 July 1977 - 31 December 1980

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COMPLETED PROJECT SUMMARY

1. TITLE: Fundamental Studies of the Structure and Chemistry of Solid Surfaces

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6. SENIOR RESEARCH PERSONNEL: Dr. Herbert Sawin

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8. PUBLICATIONS:

"A Molecular View of Diffusion and Reaction in Porous Catalysts," R.P. Merrill, Journal of Catalysis, 50, 384 (1977).

"Broad-Frequency Chopper with Adjustable Duty Cycle," H.H. Sawin, D.D. Wilkinson, W.M. Chan, S.Smiriga and R.P. Merrill, J. Vac. Sci. Tech., 14, 1205 (1977).

"Reply to Comments of CFSO-BEBO Approach," R.P. Merrill and W.H. Weinberg, Journal of Catalysis, 51, 296 (1978).

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"Chemisorption and Reaction of NH_3 on Ni(111)," C.W. Seabury, T.N. Rhodin, R.J. Purtell, and R.P. Merrill, Surface Science, 93, 117 (1980).

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"Adsorbate structures from Angle Resolved Photoemission: NH_3 on Ir(111)," R.J. Purtell, R.P. Merrill, C.W. Seabury and T.N. Rhodin, Phys. Rev. Letters, 44, 1279 (1980).

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"Concentration Profiles in Impregnation of Porous Catalysts: Nickel on Alumina," M. Komiyama, R.P. Merrill and H.F. Harnsberger, Journal of Catalysis, 63, 35 (1980).

"Angularly Resolved Temperature Programmed Decomposition: Nitrogen Emission from the Decomposition of Hydrazine on Ir(111)," H.H. Sawin and R.P. Merrill, J. Chem. Phys., 73, 996 (1980).

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"A Semi-Classicl Trajectory-Based Calculation of the Multiple Scattering Problem," A.P. Jauho, M. Cohen, J. Wilkins and R.P. Merrill, to be published in the Proceedings of the Conference on Determination of Surface Structures by LEED," P.M. Marcus and F. Jona, Editors.

"Molecular Orbital Calculations of Atomic Hydrogen Chemisorption on the Beryllium(0001) Surface," G.B. Hoflund and R.P. Merrill, Journal of Physical Chemistry, 85, 2037 (1981).

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"Angular Orientation of NH_3 on Ni(111) by Low Energy Photoelectron Scattering," W.M. Kung, C.H. Li, S.Y. Tang, C.W. Seabury, K. Jacobi, T.N. Rhodin, R.J. Purtell and R.P. Merrill, [illegible] Rev. Letters, 47, 931 (1981).

"A Kinetic Study of Hydrazine Decompos[illegible] Ir(111) by Molecular Beam Scattering and Temperature Programmed De[illegible]tion," H.H. Sawin, Ph.D. Thesis Cornell University (1980).

"Ammonia Chemisorption on Ir(111)," R.J. Purtell, Ph.D. Thesis, Cornell University (1980).

"Impregnated Nickel on γ Alumina Catalyst: Catalyst Design and Impregnation," M. Komiyama, Ph.D. Thesis, Cornell University (1980).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The primary objective of the work supported by this grant was to examine the decomposition of hydrazine on iridium from a molecular point of view. Since this reaction proceeds very rapidly, reaction probabilities near unity, it is impossible to measure intrinsic kinetics by traditional means at pressures near one atmosphere. Accordingly, this work used reactive molecular beam scattering and temperature programmed desorption techniques. A complimentary approach was to use modern spectroscopic techniques to identify the electronic structure and bonding modes of the surface intermediates in the reaction sequence. Auger spectroscopy, X-ray Photoelectron Spectroscopy, and Ultraviolet Photoelectron Spectroscopy were used.

The technological objective of this work was to develop enough understanding of the decomposition mechanism to suggest ways of studying the catalyst de-activation and poisoning and to provide guidance on how to develop more stable catalysts. In order to integrate the findings of our fundamental decomposition studies into this technological objective we also examined the problem of reaction and diffusion in porous catalysts from a molecular view and did some work to identify the mechanisms which control the radial concentration profiles which develop when catalysts are made by aqueous impregnation of porous oxide supports.

Using the combination of reactive molecular beam scattering and temperature programmed desorption it has been possible to determine most of the salient features of the reaction sequence of hydrazine decomposition on the (111) face of iridium. The reaction "lights-off" at 200°K to a reaction probability of 0.95 or greater and stays nearly constant up to 1500°K, confirming the remarkable reactivity suggested by the conventional catalytic work. From 200°K up to 500°K the primary decomposition products are NH_3 and N_2. Above 600°K little NH_3 is produced.

There are at least three parallel channels for the production of NH_3 in the reaction sequence. all three are simultaneously evident in the experimental transfer function between 500°K and 600°K. Only two are absorbed at temperatures ca. 300°K where the catalyst used in thruster engines is required to "light-off". One has a time constant of several seconds and a branching ratio of 0.95. The other channel has a time constant of ca. 1 m sec., but since it produces only 5% of the NH_3 product it could never be studied in technological catalysts using standard catalyst testing procedures.

Catalyst deactivation causes disintegration of the catalyst particles in thruster service. This is caused by imbibation of the liquid hydrazine into the pores of the pellet. If the catalyst does not light off within 10^{-3} sec. there is too much liquid uptake and the pressure build-up within the interior of the catalyst exceeds the tensile strength of the pellet before the liquid can be pumped back out of the catalyst. Clearly, then, it is the 5% branch of the decomposition reaction that is responsible for the 10^{-3} sec. light off, not the main channel which requires several seconds. This is certainly the <u>most significant technological</u> finding of the work. It means that one must study this fast branch to identify the caues of catalyst deactivation and to develop stragetles for improving catalyst stability. This will require carefully designed <u>time response studies in the absence of mass transport limitations</u> and will <u>not be possible using steady-state measurements</u>.

Initially, hydrazine adsorbs dissociatively onto the clean iridium surface to produce adsorbed hydrogen atoms and a di-adsorbed di-imide. Adsorption into this state is irreversible and TPD of this species yields NH_3 and N_2. A reversibly adsorbed hydrazine can adsorb onto this di-imide. The decomposition of the di-imide-hydrazine complex to give gas phase N_2 and two adsorbed NH_3 comprises one of the decomposition branches, i.e. the slow branch at 300°K. The fast branch at 300°K passes through an NH_2 adsorbed species which adds adsorbed H to give NH_3 which subsequently desorbs. The third branch results from successive dehydrogenation of a mono-adsorbed di-nitrogen species and subsequent addition of hydrogen to non-adsorbed nitrogen to give a sort of nitrogen analog of adsorbed methyl isocyanide, $H_3N{-}N{\equiv}Ir$. This species then decomposes to give gaseous NH_3 and adsorbed N atoms. This complex reaction sequence has within it fourteen elementary steps. The studies have been able to measure the rate of 13 of these fourteen steps at at least one temperature. Four of the elementary rates have been measured over a sufficiently wide temperature range that both pre-exponentals and activation energies have been determined. The role of surface diffusion is evident in the steps involving adsorbed hydrogen addition and in the slow branch passing through the hydrazine/di-imide complex.

Spectroscopic evidence for N_2H_4, NH_2, NH_3 and N surface intermediates has been found. Adsorbed NH_3 has been characterized most completely. NH_3 adsorbs through the nitrogen lone pair with the hydrogen triad parallel to the surface. The N-H bonding orbitals are barely shifted by adsorption though the lone pair is stabilized by adsorption. The amount of stabilization of the lone pair on different metals correlates with its chemisorption binding energy. The work function change is very large, -3 eV on a saturated overlayer. This is too large to be attributed only to orientation of the gas phase dipole and implies charge transfer from the lone pair into the iridium metal. The chemisorption binding site is one of the three fold hollows on the (111) surface and the NH_3 molecule is rotationally oriented by adsorption. There is also a density driven phase transition at ca. 120°K which nucleates a (2x1) surface structure that produces a strong dispersion in the the energies of the 1e N-H bonding orbitals as two dimensional energy bands are formed.

Ammonia TPD exhibits three desorption states, but no decomposition to Nitrogen when the surface is scrupulously clean of oxygen. These same three peaks are present, with some changes in relative intensity, when hydrazine is decomposed by temperature programming.

In aqueous impregnation it has been demonstrated that one can control the radial concentration profiles of metal as it is deposited on the interior pore walls of a macroscopic support pellet by adjusting the adsorptivity of the species. A model has been developed which adequately predicts changes in the profiles. One can obtain a uniform profile, a profile where most of the metal is deposited near the exterior of the surface of the catalyst pellet, a sub-surface impregnation, or a band of metal may be deposited with the exterior being free of metal and the center of the pellet also being free of metal. The concepts were demonstrated using nickel solutions impregnated into aluminum spheres. Measurements were made using x-ray floursecense in an electron microprobe.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The objective of this project was to examine the decomposition of hydrazine on iridium from a molecular point of view. An understanding of the decomposition reaction is critical to the development of catalytic thruster engines which are less prone to catalyst deactivation and poisoning than present devices. The surface techniques employed to follow the reaction included reactive molecular beam scattering, temperature, programmed desorption, Auger spectroscopy, X-ray photoelectron spectroscopy, and ultraviolet photoelectron spectroscopy. These

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) techniques allowed determination of most of the salient features of the reaction sequence of hydrazine decomposition on the (111) face of iridium. At least three parallel channels for the production of NH_3 were found. Branching ratios and time constants were determined for each of these reactions. The results clearly indicated which reaction mechanism is responsible for thruster "lights-off" as well as indicating a mechanism for catalyst decomposition and break-up.

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