Eleventh DOE/BES Heterogeneous Catalysis and Surface Science Meeting

Rockville, Maryland
August 16-18, 2000

Preface

This report summarizes a wide range of research programs which have both potential and current impact in the area of heterogeneous catalysis and are supported by the Department of Energy's Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences and the Materials Sciences and Engineering Divisions. The participants at this meeting include researchers from Department of Energy (DOE) National Laboratories, and university researchers who currently receive DOE support for catalysis-related research. They are joined by representatives from DOE headquarters and several invited guests from within the catalysis community.

This is the eleventh in this series of meetings, the first in four years, to foster technical discussion between researchers and to provide an opportunity to establish interactions and collaborations between scientists with similar interests. An additional purpose of the meeting is to provide a forum for active researchers to discuss current and future problems in catalysis as well as possible future directions. The informal interactions on these topics during the course of the meeting comprise an important meeting objective.

The conscientious and able efforts over many months of Professors Raul Miranda at the University of Louisville and Curt Conner of University of Massachussetts in helping to arrange and host this meeting are gratefully acknowledged.

Dan Melamed

August 2000

Eleventh BES Meeting on Heterogeneous Catalysis and Surface Science

Tuesday August 15

Arrival

Wednesday August 16

7:00-8:00 Poster Setup/Breakfast

8:00-8:30 Conference Opening Remarks

I. Fundamental techniques

Spectroscopy I: Surface Spectroscopy and Imaging of Model Catalysts

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8:45 - 9:00	Chemistry of Complex Organic Energy Resources: Molecular Dynamics in Model Systems Having Constrained Lateral Diffusion" M.E. Sigman - OAK RIDGE NATIONAL LABORATORY	2
9:00 - 9:15	Infrared Spectroscopy of Metal Clusters and Cluster-Adsorbate Complexes Michael A. Duncan - UNIVERSITY OF GEORGIA	3
9:15 - 9:30	Oxide-Supported Metal Catalysts: Energetics Controlling Particle Size and Chemisorption/Catalytic Properties Charles T. Campbell - UNIVERSITY OF WASHINGTON	4
9:30 - 9:45	Scanning Tunneling Microscopy Study of the Structure and Stability of Reactive Sites on Oxide Catalyst Surfaces Eric I. Altman - YALE UNIVERSITY	5
9:45 -10:00	Chemistry of Bimetallic and Alloy Surfaces Bruce E. Koel - UNIVERSITY OF SOUTHERN CALIFORNIA	6
10:00-10:15	Chemical Dynamics at Surfaces Mike White - BROOKHAVEN NATIONAL LABORATORY	7
10:15-10:30	Correlations Between Surface Structure and Catalytic Activity/Selectivity D. W. Goodman - TEXAS A&M RESEARCH FOUNDATION	8

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Modeling and Calculation

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11:15-11:30	Modeling NO_x Catalysis by Cu-Exchanged Zeolites James B. Adams - ARIZONA STATE UNIVERSITY	10
11:30-11:45	Computational Chemistry Applications in Heterogeneous Catalysis John B. Nicholas - PACIFIC NORTHWEST NATIONAL LABORATORY	11
11:45-12:00	First-Principles Studies of Chemical Properties of Metal and Oxide Surfaces Ruqian Wu - CALIFORNIA STATE UNIVERSITY AT NORTHRIDGE	12
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2:15-2:30	In-situ UV Raman Spectroscopy in a Fluidized Bed Peter C. Stair - NORTHWESTERN UNIVERSITY	19
2:30-2:45	Progress In Applications of High Resolution Solid State NMR to Catalysis M. Pruski - AMES LABORATORY	20

Synthesis and Design of Catalytic Materials

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II. Major catalyst types

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11:30-11:45	Selective Oxidation of Hydrocarbons Over Mixed Metal Oxides: Spectroscopic and Kinetic Characterization of Sol Gel and Combinatorial Catalysts Glenn L. Schrader - AMES LABORATORY	50
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5:45-6:00	Sulfur Interaction with Metal Surfaces Jan Hrbek- BROOKHAVEN NATIONAL LABORATORY	70
6:00-6:15	Desulfurization Processes on Oxide and Sulfide Surfaces Jose A. Rodriguez-BROOKHAVEN NATIONAL LABORATORY	72
6:15 -6: 30	Novel Catalysts for Advanced Hydroprocessing: Transition Metal Phosphides S. Ted Oyama- VIRGINIA POLYTECHNIC INSTITUTE & STATE UNIVERSITY	74
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Concluding Talks

Chemical Bond Activation On Surface Sites Generated Photochemically

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The production of nascent surface sites capable of activating chemical bonds in a range of molecules has been achieved by photochemical means. The direct photodesorption of a CO ligand from the $Rh(I)(CO)_2$ /Al_2O_3 species has been observed, and the coordinatively unsaturated Rh site produced by this process has been found to activate the C-H bond in alkanes, the H-H bond in H_2, the O=O bond in O_2, and the C=O bond in CO_2. This site is not capable of activating the N_2 molecule, and a substitution reaction producing $Rh(I)(CO)(N_2)$ and $Rh(I)(N_2)(N_2)$ is observed. The photochemical process has been studied on the dispersed catalyst using transmission IR spectroscopy as well as UV-VIS spectroscopy, and the nature of the direct electronic activation leading to active site production has been probed. The work as a whole is closely connected to similar chemistries observed in homogeneous phase using organometallic target molecules.

Chemistry of Complex Organic Energy Resources: Molecular Dynamics in Model Systems Having Constrained Lateral Diffusion

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The objective of this program is to conduct basic research that provides new molecular level knowledge of the chemical structure and reactivity of complex carbon systems typified by fossil and renewable organic energy sources such as coal, petroleum, oil shale, lignin and biomass. The knowledge gained from this research contributes to the scientific foundations of novel, environmentally responsible, energy efficient processes for the utilization of hydrocarbon resources as a source of fuels, chemicals and advanced materials. The kinetic and mechanistic information derived from these studies provides insight into chemical transformations under diffusional constraints that are important in the processing of cross-linked macromolecular organic systems. The work presented will focus on newly initiated photochemical and photophysical studies of the impact of restricted diffusion on the rates and energetics of hydrogen atom abstraction reactions. Fluorescence anisotropy measurements are being employed to provide new insights into the molecular dynamics of silica-supported moieties in organic energy resource model systems. These experiments are designed to measure rates of molecular reorientation for surface-attached (lateral diffusion restricted) chromophores. The rates of reorientation will be coupled with rates of hydrogen atom abstraction to provide a more complete picture of radical center migration in diffusionally restricted systems. Free-radical clock rearrangements and direct observation through transient spectroscopic techniques will measure hydrogen atom abstraction rates.

Infrared Spectroscopy of Metal Clusters and Cluster-Adsorbate Complexes

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Metal atom clusters have exciting applications in heterogeneous catalysis, which has enormous importance for the conversion of fossil fuels into useful chemicals. Our research explores the fundamental properties of nanoscale metal clusters and crystallites. New techniques have been developed and are under development to probe the vibrational spectroscopy of these clusters as well as complexes containing metal clusters with simple adsorbates. Up-to-date details of this new work will be presented.

In the first area, metal clusters containing up to 200 atoms are probed with the new technique of IR-REMPI spectroscopy using far infrared radiation from the "FELIX" free-electron laser. Metal carbide clusters of titanium and vanadium have recently been studied to demonstrate this methodology. New experiments extend this work to study niobium-carbide clusters and metal oxide clusters of magnesium, aluminum and titanium. In the IR-REMPI method, gas phase clusters are excited on resonance with their vibrational spectrum, and subsequent multiphoton absorption results in "thermionic emission" of an electron. The corresponding positive ions are detected in a mass spectrometer as a function of the laser wavelength, providing a size-selected vibrational spectrum for the cluster. Vibrational modes associated with surface phonons for the clusters are detected, which can be compared to previous EELS spectra of the bulk materials or to IR spectra of thin films.

In the second new area, infrared OPO lasers are employed in the mid-IR region (2000 to 4500 cm^{-1}) to probe the vibrational modes of adsorbate molecules interacting with metal clusters. Cluster-adsorbate complexes are produced in the gas phase, size selected with mass spectrometers, and detected via resonance-enhanced photodissociation spectroscopy. This new area is under development, and the first results will be presented.

Oxide-Supported Metal Catalysts: Energetics Controlling Particle Size And Chemisorption / Catalytic Properties

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Oxide-supported metal catalysts are important in many facets of energy technology. In this project, we address the relationships between the energetic stability of late transition metal particles on oxide supports and their structural, electronic, chemisorption and catalytic properties. Oxide-supported metal catalysts have been studied here using well-defined surfaces involving vapor-deposited metal films on single-crystal oxides. Angle-resolved Xray photoelectron spectroscopy (ARXPS), low-energy He ion scattering spectroscopy (ISS), low-energy electron diffraction (LEED), work function, and band-bending measurements and temperature programmed desorption (TPD) were used to characterize the resulting structures formed and their chemisorption properties. The thermal thickening (sintering) kinetics of metal islands have also been measured using temperature-programmed ISS. Metal adsorption calorimetry was performed using a chopped atomic beam of metal vapor, which adsorbs onto an ultrathin single crystal's surface, causing a transient temperature rise. This heat input is detected by a pyroelectric polymer ribbon, which is gently touched to the back of the crystal during calorimetry. The differential heat of adsorption is thus measured as a detailed function of coverage up through multilayer coverages. From the integral heat of adsorption, we can also calculate the adhesion energy of the metal film to the oxide and its interfacial energy. An adhesion energy for Cu to clean MgO(100) of 220±30 $\mu J/cm^2$, for example, was determined in this way. Techniques that provide adhesion energies for films at clean, well-defined surfaces are *not* otherwise available, to our knowledge.

The effects of flux, temperature and defect density on the metal particle morphology were studied for $Au/TiO_2(110)$ and Cu/ZnO(0001) and fitted to an atomistic kinetic model. Their measured sintering kinetics are now being modeled.

The bonding of late transition metals to support oxides is weak, so that, when metal particles with 100% dispersion (in the form of 2D rafts) can be prepared, they chemisorb molecules more strongly than do thicker (i.e., 3D) metal particles. On $TiO_2(110)$, for example, 2D Au islands adsorb oxygen adatoms much more strongly than do thick 3D Au clusters. This implies that ultrathin gold particles should be able to dissociatively adsorb O_2 more readily than large gold particles. The association reaction ($CO + O_{ad} \rightarrow CO_2$) gets faster as the oxygen adsorption energy decreases (with Au island thickness), as expected based on Brönsted relations.

We have also addressed the effects of surface chlorine on catalyst dispersion and on the reaction pathways and kinetics of adsorbed formate on model Cu/ZnO(0001) and Pt/ZnO(0001) catalysts. Pre-adsorption of chlorine facilitates metal particle agglomeration, and alters the decomposition selectivity of Zn-bound formate to favor dehydrogenation.

Scanning Tunneling Microscopy Study of the Structure and Stability of Reactive Sites on Oxide Catalyst Surfaces

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Metal oxide surfaces play an important role in many processes central to efficient resource utilization and pollution control. Improvements in the selectivity and activity of oxide catalysts have the potential to reduce emissions of toxic gases, to improve the efficiency of the chemical industry, and to allow the use of less expensive feedstocks in the chemical industry. Despite the importance of oxide catalysts, the relationship between catalytic activity and structure remains a subject of debate. Therefore, we have been characterizing the structure and reactivity of active sites on oxide surfaces using scanning tunneling microscopy (STM) along with temperature programmed desorption (TPD) and other standard surface characterization techniques. We have been focusing on the (001) surfaces of the isostructural oxides WO_3 and β-MoO_3. By varying the surface preparation conditions, a number of different surface structures can be prepared. For WO_3(001) these include an atomically rough surface, a c(2×2) surface with half the terminal oxygens removed, (2×2), c(4×2) and c(6×2) surfaces with ¾ of the terminal oxygens removed and half the surface W ions reduced from +6 to +5, and a (1×1) surface with all the terminal oxygens removed and all the surface W ions reduced to +5. Thus by comparing the reactivity of these surfaces towards a series of alcohols, we are determining the effect of cation reduction and terminal and bridging oxygens on the catalytic pathway. Further, by comparing WO_3 and β-MoO_3 we are determining the effect of the cation without changing the structure. We have found that the WO_3 (001) c(2×2) surface readily adsorbs methanol, 1-propanol, 2-propanol, and t-butanol. All the alcohols adsorb molecularly at 300 K and dissociate to form an alkoxide at 400 K; the primary, secondary, and tertiary alkoxides react to form the corresponding alkene, indicating that the c(2×2) surface exhibits only dehydration activity. The alkene desorption temperatures decreased in going from the primary to the secondary to the tertiary alcohol, indicating that the desorption is limited by the rate of C-O bond cleavage of the adsorbed alkoxide. STM images of 1-propoxide showed that the alkoxide forms on the c(2×2) terraces above the exposed W^{+6} ions. The images also revealed no preference for the alkoxide to bond to steps or other defects on the surface. Further, we have demonstrated that the alkoxide can be removed from the surface with the STM tip, opening up the possibility of directly determining the structure of the underlying adsorption site for oxides in which isolated defects dominate the catalytic behavior of the surface.

Chemistry of Bimetallic and Alloy Surfaces

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Supported metal heterogeneous catalysts are central to developing new and improved energy technologies and mitigating environmental impacts of energy use. Metal catalysts usually, if not always, involve more than one metal component. However, while we understand fairly well chemical reactions that occur on individual metal surfaces, there is little fundamental knowledge about how surface composition and structure of multi-metal catalysts give rise to the superior properties of such catalysts over those of the single-metal components. The objectives of our research are to define the overall chemical reactivity of bimetallic alloys and clarify the role of a second metal in altering surface chemistry and catalysis on bimetallic surfaces. This will aid developing general principles for understanding the reactivity and selectivity of bimetallic catalysts. Several alloys have been investigated, but the focus of the current work is on Pt-Sn due to its importance and potential for carrying out selective hydrogenation and dehydrogenation reactions. Our research plan is to carry out fundamental studies of primarily hydrocarbon reactions on well defined, *ordered* surface alloys of Sn with Pt that can be prepared by the controlled vapor deposition of Sn onto single crystal Pt substrates. Spectroscopic studies of hydrocarbon chemisorption and reaction in UHV on these surfaces reveal changes that occur in adsorption, bonding, and reaction selectivity as the reactive Pt ensembles available are steadily reduced to include isolated 3-fold Pt sites, 2-fold Pt sites, and single Pt atoms. In parallel with these studies, we are measuring catalytic reaction kinetics over these same surfaces at higher (1-760 torr) pressures to understand how the composition and structure of Pt-Sn alloy surfaces affect activity and selectivity in hydrocarbon catalysis. Measurements of activation energies and reaction orders for catalytic reactions over alloy model catalysts are carried out in a microreactor that is attached to a fully instrumented UHV chamber. A transfer-rod enables us to prepare ordered Pt-Sn alloys in UHV, carry out the catalytic studies, and characterize the surfaces following reaction. Our focus up to this point has clearly been on surface-science type of investigations. These play an essential role in understanding the catalysis occurring over these surfaces by providing measurements of the rates of elementary reaction steps and identifying possible reaction intermediates. This helps elucidate and simplify mechanisms proposed to explain high-pressure catalytic reactions.

Chemical Dynamics at Surfaces

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The aim of this research program is to explore the internal state and translational energy dependence of elementary activation, association and oxidation reactions on transition metal surfaces that are important in energy-related catalysis. Our approach is based on measurements of the energy and quantum-state distributions of desorbed products which reflect the mechanism of the desorption process, and in favorable cases, can be used to infer dynamics on the surface-bound transition state potential. This approach is well suited for probing the reaction dynamics of simple systems (e.g., H_2, O_2, N_2, CO, NO, CO_2, H_2CO) which are ubiquitous in catalytic processes such as reforming, epoxidation and feedstock chemical production. Photoexcitation leading to surface heating (infrared light) or photodissociation (UV light) is also being used as an alternative means for activating surface reactions with some control over reaction intermediates, kinematics, time-scales and rates.

Current studies are centered in three areas: (1) fundamental studies of photo-induced desorption on metal surfaces; (2) investigations of oxygen recombination and selective oxidation reactions on silver surfaces; (3) exploring the use of photoexcitation for inducing novel surface reactions at low surface temperatures. Highlights of this work are summarized below:

- A previously unknown non-thermal desorption mechanism was characterized in state-resolved studies of IR-induced (1064 nm) desorption of weakly bound adsorbates (CO, N_2, Kr) on Ag(111). (Rao, *et al*, *J. Chem. Phys.*, **109**, 8016 (1998)).
- The kinetics of the partial oxidation of methanol were measured *in real time and under collision free conditions* using a novel Ag-membrane reactor and a differentially-pumped mass spectrometer for product (formaldehyde) detection. (Beuhler, *et al*, *J. Phys. Chem.*, submitted).
- The dynamics of the O-atom recombination reaction on a polycrystalline Ag surface were investigated in the first use of state-resolved spectroscopy for detecting O_2 resulting from a surface reaction.
- State-resolved detection of desorbed CO was used to investigate the UV-induced photodissociation dynamics *and* photo-polymerization kinetics of formaldehyde on Ag(111) . (Rao, *et al, J. Phys. Chem.* **102**, 9050 (1998)).

Future work will continue to explore the use of photoexcitation for inducing otherwise thermal reactions via photodissociation or IR laser-induced thermal heating of co-adsorbed species at low surface temperatures (20-100 K). These studies will focus on the dissociative adsorption (activation) of N_2, O_2, NO, CO_2 and CH_4 on transition metal surfaces (Ag, Pd, Ni) which represent elementary reaction steps in oxidation, De-NO_x and dry reforming reactions. Reactivity studies using the Ag-membrane reactor will be extended to the epoxidation of ethylene with the goal of obtaining mechanistic and rate information. New experimental capabilities include a 2-D ion-imaging spectrometer for obtaining the spatial distribution of desorbing neutral molecules and a molecular beam scattering apparatus. The latter will be used in concert with state-resolved measurements to investigate the translational energy dependence of sticking and reaction, with specific application to SO_2 reactivity on pure and metal-promoted oxides (Mg, Zn) related to sulfur removal in combustion emissions (De-SO_x).

Correlations Between Surface Structure and Catalytic Activity/Selectivity

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The project objective is to address those issues that are keys to understanding the relationship between surface structure and catalytic activity/selectivity. Of primary concern in the current studies are the origins of the unique catalytic properties of nano-metal clusters, particularly those of supported gold catalysts for partial oxidation reactions. The experimental approach utilizes a microcatalytic reactor contiguous to a surface analysis system, an arrangement allowing in vacuo transfer of the catalyst from one chamber to the other. Surface techniques being used include Auger (AES), UV and X-ray photoemission spectroscopy (UPS and XPS), ion scattering spectroscopy (ISS), temperature programmed desorption (TPD), low energy electron diffraction (LEED), high resolution electron energy loss spectroscopy (HREELS), infrared reflection-absorption spectroscopy (IRAS), and scanning probe microscopies (UHV-STM, AFM). Currently the preparation, characterization, and determination of the catalytic properties of ultra-thin metal and metal oxide films are being explored. Specifically, the program is proceeding toward three goals: (1) modeling supported metal catalysts using ultra-thin planar oxide surfaces; (2) investigating the unique catalytic properties of ultra-small (<3nm), supported metal (e.g. Au, Ag, Cu) clusters; and (3) establishing a correlation between the electronic and reactivity properties of ultra-small, supported metal clusters.

Recent Representative Publications:

1. M. Valden, X. Lai, and D. W. Goodman, Science, 281(5383), 1647-1650 (1998).
2. M. Valden, S. Pak, X. Lai and D. W. Goodman, Catalysis Letters, 56, 7-10 (1998).
3. X. Lai, T. P. St. Clair, M. Valden and D. W. Goodman, Progress in Surface Science, 59, 25-52 (1998).
4. Q. Guo, W. S. Oh and D. W. Goodman, Surface Science, 437, 49-60 (1999).
5. Q. Guo, S. Lee and D. W. Goodman, Surface Science, 437, 38-48 (1999).
6. M. A. Brookshier, C. C. Chusuei and D. W. Goodman, Langmuir, 15, 2043-2046 (1999).
7. C. C. Chusuei, M. A. Brookshier and D. W. Goodman, Langmuir, 15, 2806-2808 (1999).
8. G. Liu, T. P. St.Clair, and D. W. Goodman, J. Phys. Chem., 103, 8578-8582 (1999).
9. X. Lai, T. P. St. Clair and D. W. Goodman, Faraday Discussions, (No. 114), 279-285 (1999),
   C. C. Chusuei, M. A. Brookshier and D. W. Goodman, Langmuir, 15, 2806-2808 (1999).

Structure Sensitivity of Surface Chemical Reactions

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Catalysis is at the center of the majority of industrial chemical transformations. The central goal of our program is to develop a fundamental understanding of how the detailed electronic structure of catalytic surfaces affects the thermochemistry of adsorption, the diffusion of adsorbates, and the kinetics of bond-breaking/bond-making events. This fundamental understanding provides critical insights for tuning catalytic activity and selectivity for a variety of chemical reactions in the desired direction. The design of new catalytic surfaces based on first principles calculations can lead to significant improvements of existing catalytic processes, accompanied with considerable energy savings and increased environmental protection.

In particular, periodic DFT calculations are used to demonstrate how *stepped* and *strained* transition metal surfaces show enhanced reactivity towards small molecules. Our studies show that stretched surfaces bind adsorbates stronger than compressed surfaces. Moreover, stretched surfaces are predicted to decrease the barrier for specific reactions, such as dissociation of small molecules. Similarly, systematic studies of several adsorbate/surface combinations suggest that stepped surfaces bind adsorbates stronger than flat surfaces. The role of the *d-band center* as the unifying underlying parameter, successfully describing changes in the chemical reactivity of surfaces for a variety of cases, including the effects of steps and strain, will be discussed. In all cases, the chemical reactivity of the surface increases as the d-band center of the clean surface moves closer to the Fermi level. As a result, the d-band center can be treated as a useful *design parameter* for tailoring surfaces to specific reactivities.

Modeling NOx Catalysis by Cu-Exchanged Zeolites

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There has been great progress in the development of new lean-burn diesel engines that promise up to 30% increased fuel efficiency over conventional automotive engines. However, the major roadblock to their implementation is the lack of a NO_x catalyst for their operating conditions. A leading candidate is Cu-exchanged ZSM-5, especially when a reductant such as hydrocarbons or ammonia is added. One of the major issues regarding these catalysts is that we do not know the reaction mechanisms that are involved in NO_x decomposition or selective catalytic reduction (SCR).

Therefore, we have concentrated on determining the reaction mechanisms which occur during the relatively simple case of NO_x decomposition, and are now working on the more complex case of SCR by ammonia. Our work has involved a detailed quantum chemical search for the possible reaction mechanisms, and a calculation of the rates of the relevant reactions. The results of those calculations of individual rates are used as input into our new macroscopic rate equation model, which can then calculate the gases that flow out of the catalyst as a function of the input gas concentration and the operating conditions (temperature and pressure). We will present our results for NO_x decomposition, and compare them with experimental measurements of reaction products as a function of temperature.

In addition, we will discuss the important role that can be played by Cu-pairs in the zeolite, as our density functional calculations have demonstrated that they are thermodynamically stable, and our statistical analysis has shown that they will occur in significant numbers under typical loading conditions.

Finally, we will discuss our preliminary work on ammonia, and our hypotheses as to what are the major reaction pathways for SCR of NO_x by ammonia.

Computational Chemistry Applications in Heterogeneous Catalysis

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The computational catalysis program at PNNL provides fundamental understanding of important catalytic processes, such the conversion of methanol to gasoline and olefins (MTG and MTO chemistry), and the elimination of pollutants from automobile exhaust (NO_X reduction and oxidation). Thus, our program provides the knowledge needed to make chemical processes more energy efficient and less polluting. Our work combines cutting-edge theoretical methods with innovative experimental techniques. In particular, we use molecular and periodic density functional methods in combination with solid state NMR to elucidate the atomic scale behavior of catalysts. Our work has largely focused on solid acids such as zeolite and sulfated zirconia, although we have also made significant progress in understanding base catalysis on MgO and other solid surfaces. This talk will focus on our most recent results in a variety of areas.

We have determined that MTG chemistry on zeolite ZSM5 goes by a "carbon pool" mechanism. After introduction of methanol into the catalyst, there is a brief period in which conversion to olefins is negligible. During this time, a stable carbenium ion is formed. Once this carbenium ion is formed, olefin production proceeds at a much-increased rate. Control experiments indicate that olefin production ceases when this carbenium ion is no longer present. The identification of the reaction induction period, and the carbenium species that acts as a "co-catalyst" or "organic reaction center" within in zeolite is a significant advance in the understanding of the MTG and MTO mechanisms. We have also been able to use theoretical methods to identify reactive species and intermediates, determine reaction barriers, and predict reaction selectivity. We have been able to "trap" the carbenium ion by co-adsorption of small, basic molecules (CO, PH_3, and others) that either are protonated by the carbenium ion or form a complex with it. The stabilities of the various possible complexes between the carbenium ion and the coadsorbates are all correctly predicted using theoretical methods and the concepts of zeolite acidity and adsorbate basicity that we have developed over the last several years. We after also done similar investigations of MTG and MTO chemistry on silicoaluminophosphates (SaPO's) and will present those results to compare and contrast the activity of the two catalysts.

Our work on sulfated zirconia has identified many complexes and reaction intermediates formed when trimethylphosphine (TMP), trimethylphosphineoxide (TMPO) and pyridine are adsorbed on the surface. Calculations of the ^{31}P and ^{15}N chemical shifts of the species we have identified agree very well with experimental NMR measurements.

We used theoretical methods to study the stability of many "alkoxy" species that are believed to form intermediates in a variety of zeolite reaction mechanisms. Contrary to common opinion, many of these species are not stable. In fact, it is likely that no alkoxy species involving tertiary carbon can be formed on zeolites. This result has important implications for our understanding of many zeolite reactions.

First-Principles Studies of Chemical Properties of Metal and Oxide Surfaces

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Oxide and metal/oxide surfaces have recently received considerable attention because of their technological importance as photocatalysts, chemical sensors and heterogeneous catalysts [1]. For example, the Au/TiO_2 system has been shown to exhibit excellent properties as a chemical gas sensor and catalyst for room-temperature CO oxidation [2]. Highly dispersed Au on supports such as oxides also exhibits an extraordinary high activity for low-temperature catalytic combustion and reduction of nitrogen oxides [3-4].

Here I review results of our recent theoretical studies [5-7] for the structural and chemical properties of various bimetallic, oxide and metal/oxide surfaces, using the highly precise full potential linearized augmented plane wave (FLAPW) method. Density functional calculations revealed significant changes in chemical properties of Cu, Ni and Au monolayers on Ta(110), W(110), Ru(0001), Re(0001), Rh(001), MgO(001) and TiO_2(110). As an exceptional case, the profile of the density of states for the surface Ni atom appears to be very stable with increase of the thickness for a Ni film grown on Pt(111). The surface core level shifts, overlayer/substrate binding strength and the chemical reactivities of the surfaces, as found experimentally [8], are strongly correlated in bimetallic surfaces. Effects of oxygen defects on MgO(001) and TiO_2(110) are also investigated.

With the generalized gradient corrections (GGA) for the density functional formula, the adsorption energy curves (vs. the distance between CO and substrates) of CO on Au(001), Au(111), Au-monolayer, MgO(001), TiO_2(110), Au/MgO(001) and Au/ TiO_2(110) are calculated. We found repulsive potential barriers for the initial CO adsorption on all the metallic surfaces. By contrast, the adsorption energy of CO decreases monotonically before the equilibrium position on both MgO(001) and TiO_2(110). Despite the weakness of the Au/oxide interaction, the CO adsorption energy curves of the Au overlayer on MgO(001) and TiO_2(110) differ strongly from those of the Au monolayer and surfaces.

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Theoretical Studies of Surface Reactions on Metals and Electronic Materials

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This research relates to two broad subject areas: catalytic processes and properties of materials. The goal is the development and application of theoretical methods that will provide a molecular level understanding of surface processes, especially energetics, adsorbate structure and reaction mechanisms. High quality solutions of the electronic structure of adsorbate-surface systems are obtained in order to allow activation barriers to be calculated and reaction mechanisms to be determined. An *ab initio* embedding formalism provides a route to the required accuracy.

Specific topics include ethylene hydrogenation on nickel and platinum and competing pathways to the reverse reaction that forms ethylene from adsorbed ethyl. Potential energy surfaces and vibrational properties of surface species are calculated and compared with experiment. Excited electronic states of CO on platinum are calculated in order to understand the shift in levels observed experimentally and field effects on the desorption of CO on interaction with STM tips. Excited states implicated in the direct optical excitation of Si-H bonds on the Si(100)-(2x1)H surface will be calculated in order to understand photodesorption experiments. Studies of the photoinduced dissociation of methyl nitrite on Ag(111) are underway. The enhanced activity of gold particles on TiO_2 in the catalytic oxidation of CO will be investigated.

New directions are being pursued in the development of theoretical methods. In order to use *ab initio* configuration interaction methods to treat extremely large electronic systems, advances in computational methods and strategies are required. The first involves an extension of previous embedding work in which large systems are partitioned into coupled regions, each treated self-consistently. The basic computational strategy has been designed and test calculations have recently been carried out. The second advance concerns new ways to handle the large amount of information required in *ab initio* CI calculations. In order for CI to remain a viable method for treating large electronic systems, it is necessary to depart from standard practices of calculating and storing integrals over basis functions. Our new approach, under active development during the past few months, makes use of the fact that smaller electronic interactions can often be expanded accurately in terms of existing densities required for other parts of the problem. There are two requirements for the approach to work: first, it is necessary to identify efficiently the set of densities that will be used to expand the density in question, and, second, it is necessary to know the accuracy of the resulting expansion. The former question is addressed by dividing the total spatial region into cells. As large electronic interactions are calculated, the basis function pairs that have been used are filled into these cells. Then, as smaller interactions are considered, the new densities are expanded in terms of the content of these cells. Rigorous electrostatic error bounds are used to judge the acceptability of the expansion. We are optimistic that the theoretical advances will greatly extend the applicability of CI calculations while maintaining the accuracy of this many-electron method.

New Solid State NMR and Diffraction Approaches for Studying Catalysts: Applications to Zeolites and Aluminum Oxides

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We have been using a combination of solid state NMR and in-situ x-ray diffraction (XRD) methods to determine the nature of some the phases that are present during the catalytic reaction, and how they change with time as the catalyst is activated and deactivated. Two projects will be discussed. In the first, work has focussed on the activation of γ-alumina for a variety of hydrofluorocarbon (HFC) and hydrochlorofluorocarbon (HCFC) isomerization and dismutation reactions[1] with gases such HCFC-22 (CF_2HCl) and HFC-23 (CF_3H). The HCFC-22 dismutation occurs via the following reactions:

$$2CHF_2Cl \rightarrow CHF_3 + CHCl_2F$$
$$2CHCl_2F \rightarrow CHClF_2 + CHCl_3$$

In situ XRD experiments were performed by heating the sample of γ-Al_2O_3 (in a sapphire capillary, gas flow cell) under flowing HCFC-22, and monitoring the reaction downstream of the catalyst bed with g.c.. The catalyst becomes active for dismutation at 300 • C, but no change is observed by XRD. At 400 • C, a phase grows in that resembles the high temperature phase of α-AlF_3. On cooling the sample, a phase change occurs and α–AlF_3 is observed at room temperature. A second sample activated at 300 • C was subsequently annealed at 400 • C in the absence of HCFC gas, and the high temperature phase of α-AlF_3 was observed to nucleate. XRD structural refinements are currently underway to investigate the phases formed during catalysis. The results are consistent with ex-situ $^{19}F/^{27}Al$ cross-polarization experiments of the phase activated at 300 • C, which show that α–AlF_3 is present, even in the samples activated at lower temperatures. The cross-polarization experiments allow us to detect small levels of fluorination, even in the presence of bulk γ-Al_2O_3. ^{19}F and ^{27}Al NMR have been used to study the mode of binding of the HCFC molecule to the γ-Al_2O_3 surface, and its subsequent reactivity.

In parallel studies, we are examining HFC and HCFC reactivity in zeolites. Here we are utilizing a number of different NMR experiments designed to probe internuclear distances (e.g., $^{19}F/^{23}Na$ CP NMR[2]) to determine how the gas molecules bind to the internal surfaces of the zeolites. Once the mode of binding and, importantly, the effect of gas binding on the structure of the catalyst have been established by NMR and in some cases by XRD[3], correlations with the subsequent reactivity (for dehydrochlorination and dehydrofluorination) can be made. Again, double resonance NMR experiments allow changes in the zeolite structure following reaction to be determined.

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Lessons from Sorption in Molecular Sieves

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Analyses of the adsorption isotherms are a primary method by which the pore structure of porous solids are characterized. Molecular sieves are developing engineered solids employed as catalysts and selective sorbents throughout the energy industries. The pore dimensions and surface areas of molecular sieves are determined by combinations of sorption, x-ray for crystalline solids and electron microscopy for the larger pore systems. The MCM-type solids present an apparently ideal, uniform-pore structure to test sorption behavior in molecular sieves. Indeed, a majority of studies of MCM materials include nitrogen sorption isotherms, surface areas and the pore dimensions calculated from them. These analyses are most often calculated based on the analysis-software present in the conventional automated sorption systems.

Figure 1: Typical normalized adsorption isotherms at 77K for two samples of MCM are shown below:

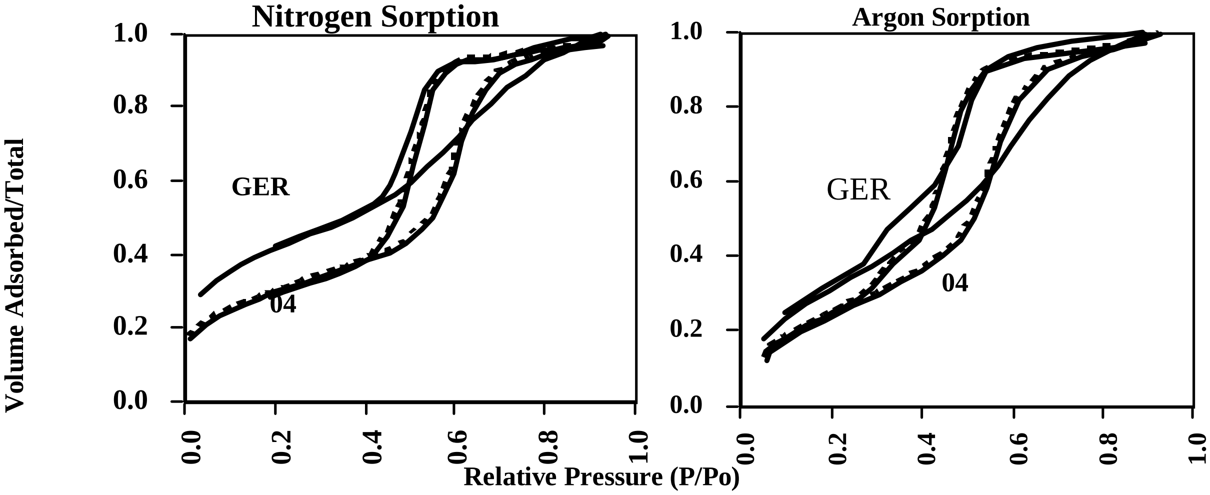
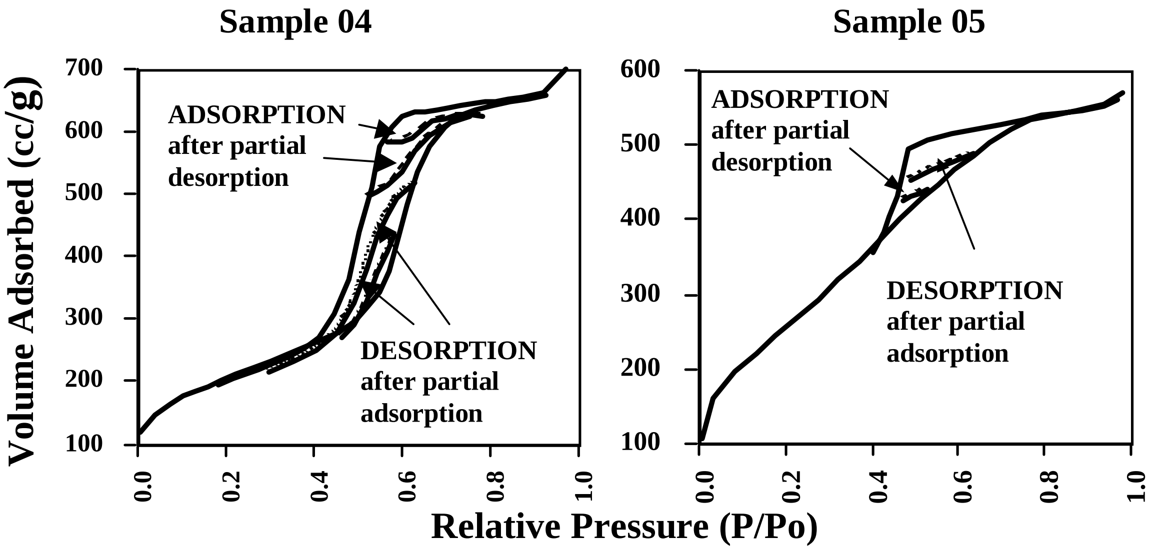


Figure 2: Examples of the scanning behaviors are illustrated below for Ar adsorption and desorption at 77K. The scanning curves are shown as dotted lines within the hysteresis loops.



Several aspects of the sorption analyses have been studied:

What model(s) should be employed to characterize multilayer sorption prior to pore filling?(1)
What are the differences between the use of N_2 or Ar @ 77, 87 or 90K for characterization by sorption?
What are the differences in analyzing the adsorption or desorption data to calculate pore dimensions? (2)
When will the "tensile strength" effect obscure the determination of pore dimensions? (3)
What are the "proper" pore dimensions of molecular sieves from X-ray analyses ?

EXPERIMENTAL

This study employed a score of MCM and zeolite samples analyzed by several sorption systems in different laboratories, including a unique high resolution sorption system(4). While the sorption data are similar, the analyses are not. The suggested modifications to the analyses of sorption data provide a more realistic characterization as well as they will result in firmer bases for the ongoing theoretical modeling of sorption in mesoporous solids.

CONCLUSIONS

We find that BJH analyses provides a reasonable approach to analyze the isotherms for the MCM family of solids. However, some modifications are needed. Specifically, the value of the Halsey exponent varies from 1/1.2 to 1/2, both of which are significantly different than the 1/3, which is employed by automatic adsorption analyses systems. Both Ar and N2 can be employed for sorption at 77K as seen above while Ar at 87K also yields similar data. Comparison of Ar isotherms at 77, 87 and 90K demonstrate that the adsorption of the desorption branch of the isotherm often give fallacious results. This is due to the "tensil strength" artefact which has been known for years(3).. The easiest way to detect this "tensil strength" artefact is also to analyze the adsorption isotherm. It should be apparent that any feature found in desorption that is not evident in adsorption should be questioned. Indeed, we conclude that analyses of the adsorption branch of the isotherms yield consistently more realistic analysis than the desorption data. This tensil strength artefact is evident for samples with pores from ~20Å to ~40Å in radius. For Smaller pores there is no hysteresis. For larger pores

We studied why hysteresis is most often evident for sorption in the larger pore MCM solids (greater than ~20Å in diameter) but not for the smaller pore samples. If the pores were indeed cylindrical and smooth, conventional analyses suggest that there should be no hysteresis. Our studies of hysteresis behaviors employed scanning (changing from adsorption to desorption or back) within the hysteresis loops to see if the current theories for hysteresis were consistent with the detailed data available from scanning studies. We found three types of scanning behavior. It was apparent that a single theory cannot explain the different types of behaviors that are evident in the data. DFT and statistical mechanics theories (5,6) predict a jump in the volume adsorbed between adsorption and desorption branches of the isotherms and we find no evidence for this in any samples. Network effects and models (a three dimensional network of pores) could be formulated to reflect much of the behavior, but these would contrast dramatically with the models presented to represent MCM-41 (cylindrical non-intersecting pores).

Finally, our studies of transport in zeolites suggested that the pore dimensions based on X-ray data present throughout the literature were incorrect. The dimensions of zeolite pores are calculated by combining the atomic positions obtained from experimental crystallographic studies with assumed values for the radii of the framework atoms. Quantum mechanics suggests that the atomic radii can be determined using a procedure called the "Norman criterion"(7) We have carried out calculations on cluster models of silica rings, which indicate that Norman radii for silicates are ~ 1.2 Å for silicon, and ~ 1.0 Å for oxygen atoms. The net effect, on average, is to increase the apparent pore diameter by twice the difference between the O ionic (1.35Å) and Norman radii, or ~ 0.7 Å.

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**Several Colleagues collaborated in this research. These include R. L. Laurence, Michael Cook, Monica MacNall, Thomas Sturgis, Michael Turner

Methanol to Olefin Chemistry on Microporous Solid Acids

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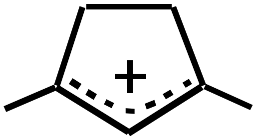
Flaring natural gas has become undesirable due to greenhouse warming, and one of the best alternatives is conversion to methanol near the well head. The US petrochemical industry hopes to use this increased methanol capacity in processes for the conversion of methanol to olefins. Natural gas then, rather than petroleum, would become the ultimate feedstock for the polyolefin industry. Methanol-to-olefin (MTO) chemistry is catalyzed using microporous solid acids, especially HZSM-5 and HSAPO-34. MTO and the closely related methanol-to-gasoline reaction have attracted a tremendous amount of fundamental study; at least 20 distinct mechanisms have been proposed, and it is fair to say that MTO/MTG is the most widely studied problem in heterogeneous catalysis.

Recently, we have made a fundamental advance in MTO/MTG mechanism studies. Our work reveals multiple roles for cyclopentenyl carbenium ions in the synthesis of hydrocarbons from methanol and dimethylether. The 1, 3-dimethylcyclopentenyl carbenium ion **1** is a major species formed in zeolite HZSM-5 by the conversion of methanol, dimethylether, ethylene or propene. In situ NMR experiments reveal that the formation of **1** in the catalyst bed is correlated with the end of the kinetic induction period for the synthesis of hydrocarbons from methanol or dimethylether. ^{13}C labels from cation **1** are incorporated in the olefins formed from methanol on a working catalyst. Theoretical studies show that cyclic dienes formed by deprotonation of 1 are also stable on the catalyst at very slightly higher energies and suggest pathways by which these dienes are methylated to species that eliminate ethylene or propene. Our work also shows that cation **1** is an intermediate in the synthesis of toluene, thus resolving an important mechanistic feature of MTG chemistry. In the case of HSAPO-34, our experimental results suggest that olefins are synthesized either by the same route or by a related mechanism involving methylaromatic compounds trapped in the cages of the catalyst.



1

Given the importance of cation **1** in MTO chemistry, we set out to better understand its chemistry. In particular, we studied the acid-base reactions of **1** with other co-adsorbed species that could either compete with **1** for the proton or react with it as nucleophiles. For seven bases with proton affinities (PA) between 142 and 212.1 kcal/mol, there was no reaction with the cation. Co-adsorption of smaller amounts of dimethylacetamide (PA = 217 kcal/mol) also produced no reaction, but with higher loadings, a proton was transferred from the carbenium ion to the base to leave the cyclic diene in the zeolite as a neutral olefin. Deprotonation was the primary reaction with co-adsorption of either pyridine (PA = 222 kcal/mol) or trimethylphosphine (PA = 229.2 kcal/mol). The experimental deprotonation enthalpy for the cation, ca. 217 kcal/mol in the zeolite, is almost idetnical to the theoretical gas phase value. Co-adsorption of either NH_3 (PA = 204.0 kcal/mol) or PH_3 (PA = 188 kcal/mol) does not deprotonate the carbenium ion; but these species do react as nucleophiles to form onium ion derivatives of the cation**.** Analogous onium complexes with pyridine or trimethylphosphine formed in lower yields due to steric constraints in the zeolite channels. Neither CO nor H_2O reacted with the cation. Density functional theory calculations of the enthalpies of the three possible states of the cation and each base yield predictions in agreement with the experimentally observed acid-base chemistry.

In-situ UV Raman Spectroscopy in a Fluidized Bed

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The characterization of heterogeneous catalysts and catalytic chemistry under reaction conditions can make a significant contribution to understanding catalytic processes used for fuels production and emission treatment. Raman spectroscopy is a particularly powerful tool for in-situ characterization because it provides information about both the catalyst and the catalytic chemistry in a single measurement. Using UV excitation, the fluorescence interference which often masks the Raman spectrum from catalyst materials can be avoided. However, the adsorbed hydrocarbons that are often of interest in catalysis are very susceptible to decomposition by the ultraviolet laser beam used in these measurements. A simple fluidized bed catalytic reactor was recently constructed in our laboratory to perform in-situ Raman spectroscopy measurements. This reactor makes it possible to create realistic reaction conditions while simultaneously minimizing sample damage from laser-induced heating and photochemistry. This reactor has been used to study 1) the adsorption of likely coke precursors, naphthalene and benzene, in a USY zeolite, 2) the formation of coke in H-ZSM5 during the methanol-to-gasoline reaction, and 3) the temperature dependent nature of chromia/alumina catalysts for alkane dehydrogenation. The results of these studies can be summarized as follows.

1) Naphthalene and benzene adsorb molecularly into the USY zeolite. Using a stationary or spinning pellet sample, the ultraviolet laser beam produces complete or nearly complete decomposition of these molecules to amorphous carbon. Using the fluidized bed technique, the Raman spectrum is characteristic of the undecomposed molecular species.

2) Raman spectra measured for H-ZSM5 under conditions of the methanol-to-gasoline reaction are consistent with the formation of conjugated olefinic species as a precursor to aromatic coke formation. Depending on the temperature the conjugated olefinic species and aromatic coke make coexist on the catalyst or the conjugated olefins may convert into aromatic coke.

3) The relative proportion of monomer, dimer, and crystalline chromia species supported on alumina changes reversibly with catalyst temperature. A new, as yet unidentified, species is also formed reversibly with increasing temperature. These results point out the importance of performing in-situ catalyst characterization.

Progress In Applications Of High Resolution Solid State NMR To Catalysis

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The long-term goal of our program at Ames Laboratory is to obtain a fundamental understanding of relevant catalytic systems and to use this knowledge to develop specific catalysts for important reactions. Currently, the research concerns oxidation reactions, oxygen-atom transfer and hydrogenation reactions. Solid state nuclear magnetic resonance (NMR) is among the primary tools used for these studies.

Investigation of materials and chemical reactions involved in heterogeneous catalysis and surface science can be greatly enhanced by the use of newly developed solid state NMR methods. We will present several new techniques that modernize the way in which solid state NMR is used to study the structure of catalytic materials or to examine the gas-phase reactions over solid catalysts. Some of these techniques employ multiple-quantum magic angle spinning (MQMAS) to remove second-order quadrupolar broadening from the spectra of half-integer quadrupolar nuclei. New approaches to MQMAS will be shown that provide enhanced sensitivity and allow for the observation of species that were previously ‘invisible’. These approaches include improved schemes for excitation, detection, data processing and data simulation. The application of these methods to catalysts will enable observation of nuclei with low abundance and low magnetogyric ratio, such as ^{17}O. A number of other two- and three-dimensional experiments will be reviewed that are used in the structural studies of catalytic materials and host-guest interactions in catalysts. For example, they provide direct inference of the connectivities between spin-1/2 (e.g. ^{1}H, ^{19}F, ^{31}P) and quadrupolar (e.g. ^{11}B, ^{17}O, ^{23}Na, ^{27}Al) nuclei in solids under high resolution conditions, including a determination of internuclear distances.

The analytical capabilities of these techniques are utilized in several important areas of the Hetero-Atom Catalysis program at Ames Laboratory. The applications include (i) study of the structure and function of both the tethered complex and supported metal components of the TCSM catalysts for enantioselective hydrogenation of arenes, (ii) study of sol-gel synthesis of vanadium oxide from peroxovanadates by using an innovative combination of solid state NMR of ^{51}V and in situ laser Raman spectroscopy and (iii) structural study of new types of micro- and mesoporous catalytic materials.

Materials Chemistry, Neutron Diffraction, Spectroscopy and Surface Science: An Overview

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The goal of this program is to develop and advance methods for the synthesis, characterization and manipulation of novel materials. A multi-disciplinary approach based mainly on neutron and x-ray scattering and thermodynamic methods is used to advance the knowledge base of unique and complex materials, especially as it relates to the adsorption of molecular films either on the external surface or contained within the cavity of a solid. We strive to develop a quantitative, molecular level description of molecule-molecule and molecule-surface interactions by collecting detailed information regarding the structure, dynamics and chemical activity. Neutron and x-ray diffraction and high-resolution inelastic neutron scattering methods are used to simultaneously monitor changes in the structure and dynamics of phase transformations and chemical reactions under realistic conditions. We are currently exploring how variations in size, chemical composition and morphology on a nanometer length scale effects the physical properties and reaction rates of these substances. We aim to develop reliable methods to tailor-make materials with specific chemical or adsorption properties.

We will present a summary view of the relevant range of scientific problems currently being addressed using neutrons. A brief description of the instruments that exist at various neutron facilities will also be included.

Fundamental Studies of the Formation of Mesoporous Synthetic Clays

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This program addresses the national need for understanding the formation of mesoporous catalysts, which can convert the large hydrocarbons in heavy petroleum crude oils to usable transportation fuels, in order to tune the mechanism more effectively. In our synthetic strategy, metal oxide gels are hydrothermally treated in the presence of large organic or organometallic templating molecules to make potential catalysts based on layered silicate or other porous oxide framework structures. The major objectives of this program are (1) to prepare in a predictable fashion layered inorganic frameworks that possess a narrow distribution of large pore sizes in the mesoporous range (2-50 nm) for catalytic applications, (2) to establish a better understanding of the gel chemistry involved, and (3) to obtain chemical and structural information concerning the surface chemistry of the resulting catalysts.

Recently we have probed the stability of the new class of mesoporous catalysts, dubbed MSCs for "mesoporous synthetic clays", which have been in development in our labs over the past two years[1]. MSCs are made by systematically employing a series of polymer templates that vary in such properties as molecular weight. The objective is to provide heterogeneous catalysts with tunable pore sizes over the range of 20-500 Å in diameter which encompasses the mesoporous region. The tests include long-term aging behavior, hydrothermal stability, and aqueous immersion stability. While the long-range mesoporous structure does not hold up well overall with time, the MSCs perform well in the latter two tests[2].

The synthetic mechanisms for clay formation are not well understood, and the addition of organic or organometallic species to a reactive sol-gel complicates the situation further. Solid state ^{13}C NMR experiments indicate that there are two separate processes in the crystallization of hectorite, with an obvious break at 10-14 hours[3]. This in agreement with previous atomic force microscopy images that suggested Ostwald ripening during the early stages, followed by simple aggregation at time progresses. Solid state ^{29}Si NMR was also employed which, together with the ^{13}C NMR experiments, has provided the best sensitivity yet attained; evidence of clay was seen by both techniques in as little as 30 minutes. In situ and ex situ small angle x-ray scattering studies of crystallizing hectorite clay also confirm that, at the length scales accessible by this technique, the major structural events occur within the first few hours of crystallization[3].

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Carbogenic Molecular Sieves for Reaction and Separation by Design: A Novel Approach to Shape Selective Super Base and Catalytic Membranes

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The research over the last two years has focussed upon three aspects of nanoporous carbons (NPC) or carbon molecular sieves—structural characterization and modeling, base catalysis with Cs/NPC and the synthesis of supported nanoporous carbon membranes (SNPCM). The structural analyses (neutron diffraction and HRTEM) and modeling make clear that NPC is logically considered to be chaotic but not random solid consisting of aromatic nanodomains. The bonding limitations imposed by an all-sp^2 give rise to considerable internal curvature and, hence, to voids with dimensions that are on the order of 0.5 nm. This is in good agreement measured pore sizes and the transport properties of the materials. Inclusion by chemical vapor deposition of metal onto NPC at low loading (~ 3 wt%) leads to a solid solution of Cs(I) $NPC^{\bullet/-}$, based upon ESR and magnetic susceptibility measurements. As loading levels rise ($\geq$ 15 wt%) the unpaired spins drop in number, indicating that spin pairing takes place within these same domains to give $Cs(I)_2\ NPC^{-2}$. The materials prepared with metal loading in this Cs concentration vicinity are catalysts for butene isomerization to produce cis-1-butene (75:1, - 25^oC), the side chain alkylation of benzene with propene at 1 atm pressure, the coupling of benzene to produce biphenyl, the coupling of acetone to isophorone, and non-oxidative attack of methane. At higher levels of cesium (circa 40wt%), we find that the underlying nanoporous carbon is rearranged spontaneously in an unprecedented reaction converting so-called non-graphitizing carbon into nanopolyhedra, "onions", "crop circles" and tubes. This reaction can take place at temperatures as low as 50^oC, but increases in rate at 350 and 500^oC. By applying the NPC precursor (polyfurfuryl alcohol, PFA) to porous stainless steel disks and tubes, supported films of NPC have been created with excellent thermal and mechanical stability as well molecular sieving properties. The SNPCM created by either spray coating or by ultrasonic deposition have been thoroughly characterized and tested for small molecule transport (O_2, N_2, He, H_2, light hydrocarbons, cyclohexane, benzene, SF_6…) Experimental results have led to analyses of the permeation process in terms of adsorption and diffusion. A technique has been developed to assess membrane thickness nondestructively via these measurements and transition state theory has been applied to predict diffusivities semi-empirically.

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Preparation of Highly Ordered Vanadium Substituted MCM-41: Stability, Acidic and Catalytic Properties

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Vanadium substituted mesoporous molecular sieves (MCM-41) were prepared and the effects of water amount, anti-foaming agent addition, pH adjustment, and Si/surfactant mole ratio were investigated. The hydrothermal and mechanical stability were tested for the pH adjusted sample (Si/surf. = 3.67 and 7.34). Catalysts were characterized by XRD, N_2 physisorption, ICP and 51V NMR. The acidic properties of synthesized V-MCM-41 were also examined by in-situ FTIR and TPD after pyridine adsorption. The addition of water into the synthesis solution did not affect the physical properties of the resulting samples. An anti-foaming agent was very effective in improving the reproducibility of sample structure. The amount of vanadium substitution into the silica framework was increased with increasing water amount and surfactant chain length. All of the incorporated vanadium was tetrahedrally coordinated in the silica framework. When the pH of V-MCM-41 was adjusted to 11 (Si/surf. = 7.34), the hydrothermal and mechanical stability were enhanced. The vanadium substituted MCM-41 formed Lewis and Brönsted acid sites. Brönsted acid sites increased with increasing vanadium content, but the amount of Lewis acid sites was constant for all samples. It is hypothesized that there is formed a constant and saturated amount of isolated tetrahedral coordination of vanadium, and they make weak Lewis acid sites. Brönsted acid sites can be made by the combination of vanadium with hydroxyl groups of free silanol and/or hydroxyl groups produced by water dissociation when the sample was pretreated at high temperature. These V-MCM-41 catalysts are active and selective for the gas phase oxidation of methanol to formaldehyde.

Porous Manganese Oxides: Preparation, Characterization, And Applications

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Our research involves fundamental chemical studies of energy production and storage. We focus on heterogeneous catalysis and generation of advanced materials. This research is related to national goals of energy efficiency, environmental protection, and conservation. Specific goals of our project are to prepare novel porous helices, lines and patterns of mixed valent manganese oxides such as octahedral molecular sieve (OMS) and octahedral layered (OL) materials, pillared octahedral layered (POL) materials, and novel 3-D systems; to characterize these systems to determine structural, compositional, thermal, electronic, surface, acid-base, and optical properties; and to optimize their catalytic properties in selective oxidations, and condensation reactions. Synthesis of these different materials is done with a variety of methods including sol-gel, hydrothermal, and phase transfer. A specific thrust has been to control particle size via the phase transfer route in order to prepare colloidal manganese oxide precursors.[1] Such precursors can be used to prepare novel wires, helices, lines, and patterns of porous manganese oxides. Control of the acidity of these layered precursor species allows intercalation of cationic oligomers between the layers to produce porous pillared systems.[2] Some unique characterization of these systems include small angle neutron scattering of sols and gels in order to study early stages of helix and pattern formation in collaboration with researchers at Argonne National laboratories;[1] and collaborative calorimetry studies of porous manganese oxides with researchers at UC Davis.[3] Recent calorimetry studies of OMS and OL systems have shown that the layered OL-1 phase is most stable and that linear relationships exist between $\Delta Hf^{o}_{(oxides)}$ and the hydration number of the charge balancing cations. Both acidic and basic sites have been shown to exist in OMS and OL systems and can be controlled by synthesis conditions. Such control of acidity is necessary in many of the catalytic reactions that are being studied in order to obtain desirable products with high yields. Optimization of cyclohexanol and cyclohexanone yields from cyclohexane over a variety of OMS, OL, and POL materials is being done. Shape selective redox oxidations of cyclohexane and larger substrates are carried out in order to study effects of pore size.[4-5] Base catalyzed condensations of nitrobenzene and aniline are being studied with all of the above-mentioned catalysts. Many of the catalysts developed at UCONN are being further tested at CK Witco for a variety of condensation reactions. Battery applications of lithium containing OMS, OL, and POL materials for use in secondary rechargeable nonaqueous batteries are in progress. Conductivity applications of helices, lines, and patterns are being studied in order to develop selective sensors.

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Combined Homogeneous and Heterogeneous Hydrogenation Catalysts. Rhodium Complexes Tethered on Silica-Supported Palladium Catalysts

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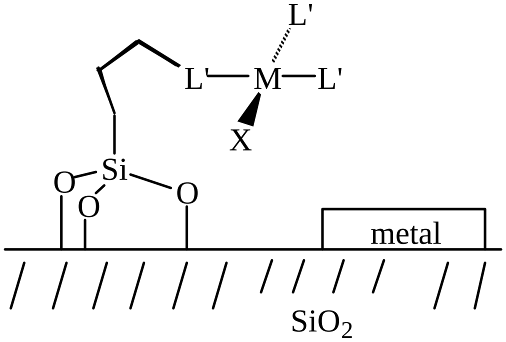
The goal of this project is to develop a conceptually new type of heterogeneous catalyst that has high activity and offers the possibility of catalyzing new industrially useful reactions. This catalyst [1] combines a silica-supported metal, e.g., Pd-SiO_2, with a homogeneous transition metal complex that is tethered to the silica surface. It was expected that such a TCSM (tethered complex on a supported metal) catalyst would function in hydrogenation reactions by activating H_2 on the supported metal, e.g., Pd-SiO_2, to generate hydrogen that spills over onto the SiO_2. This spillover hydrogen would then be available for transfer to an unsaturated substrate that is activated by binding to the tethered transition metal complex.



Conceptual illustration of a catalyst consisting of a tethered complex on a supported metal (TCSM)

In order to test the viability of this catalyst concept, we prepared a series of TCSM catalysts by tethering to Pd-SiO_2 the following square planar Rh complexes: $RhCl(CO)_2[Et_2N(CH_2)_3Si(OMe)_3]$ (Rh-NEt_2), $RhCl(COD)[H_2NCH_2CH_2NH(CH_2)_3Si(OMe)_3]$ (Rh(COD)(N-N)), $RhCl(CO)[Ph_2P(CH_2)_3Si(OEt)_3]_2$ (Rh-P), $Rh_2[\mu\text{-}(CH_2)_3Si(OMe)_3]_2(CO)_4$(Rh-S), $RhCl(CO)[C\equiv N(CH_2)_3Si(OEt)_3]_2$ (Rh-CNR_2) and $RhCl[C\equiv N(CH_2)_3Si(OEt)_3]_3$ (Rh-CNR_3). By diffuse reflectance IR spectroscopy, it was established that the Rh-CNR_2 and Rh-CNR_3 complexes retained their square [planar structures after tethering to the surface.

The activities of these TCSM catalysts were examined in the hydrogenation of toluene to methylcyclohexane under the mild conditions of 40°C and 1 atm of H_2 pressure [1-4]. Among the many comparison studies performed were those designed to determine the importance of both the tethered complex and the supported metal. All of the TCSM catalysts show enhanced activity as compared with those of just the supported metal (Pd-SiO_2) or the complex tethered on just SiO_2. In some cases, the activity is more than 10 times faster.

The durabilities of the TCSM catalysts vary depending on the tethered complex. Among the durable catalysts is Rh-CNR_3/PdSiO_2 which has the same activity in the third cycle of toluene hydrogenation as it had in the first. Over these 3 cycles during 82.5 h of use, the total turnover was 21,000 mol H_2/mol Rh.

Although it has not been established whether these arene hydrogenation reactions proceed by a hydrogen spillover mechanism or by some other process, it is clear that these TCSM catalysts are more active than either the supported metal or the tethered complex separately. We have also observed [5] that a tethered Rh-bipyridyl complex on Pd-SiO_2 catalyzes the hydrodefluorination of fluorobenzenes. Thus, the incorporation of a wide range of tethered homogeneous catalysts and supported metals might permit the design of TCSM catalysts for a variety of reactions.

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Molecular Design And Synthesis Of Heterogeneous Catalysts

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We have developed a non-aqueous, molecular precursor approach to the preparation of mixed-element oxides, which appears to allow a greater level of molecular-level control over the nanostructure of the resulting materials. This approach, which we refer to as the thermolytic molecular precursor method, has been used to obtain highly dispersed mixed-element oxide materials. Recently, we have used this method to prepare a series of VO_X/ZrO_2 catalysts for the oxydehydrogenation of propane, which are superior to those obtained by conventional means in several respects. The synthetic method involves the cothermolysis of $OV(O^tBu)_3$ with varying amounts of $Zr(OCMe_2Et)_4$ in *n*-octane, and subsequent calcination. The materials obtained have high surface areas, and were thoroughly characterized by powder X-ray diffraction, Raman, DR-UV-vis, X-ray absorption, and NMR spectroscopies. Studies of the crystallization behavior of these materials indicate that an initially formed amorphous and highly dispersed phase undergoes phase separation upon heating, with nucleation and growth of zirconia nanocrystals. As this occurs, the vanadia species migrate to the surface of the zirconia particles, and remain well dispersed. Depending on the vanadium loading, it is possible to observe single-site VO_X, oligomeric VO_X, or ZrV_2O_7. The vanadia-zirconia materials derived from alkoxides have improved dispersions of the VO_X species compared to analogous samples prepared by more traditional methods. The new materials demonstrated catalytic activities and intrinsic selectivities as heterogeneous catalysts for propane oxidative dehydrogenation that were markedly improved over materials prepared by wet impregnation. It has also been found that certain molecular precursors are useful for introduction of surface-attached catalytic species. Thus, the use of $Ti[OSi(O^tBu)_3]_4$ for introduction of titanium species on silica yielded catalysts that were highly active for the epoxidation of cyclohexene.

Effects Of Supports On Metal Complexes And Clusters: Structure And Catalysis

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We report effects of supports on the structure, reactivity, and catalytic properties of structurally well-defined metal complexes and clusters. Understanding of the metal–support bonding and structure has emerged most clearly from investigations of supported mononuclear metal complexes, $Re(CO)_3$ and $Rh(CO)_2$, on MgO powder and dealuminated zeolite Y, respectively. Bonding of the former to dehydroxylated and to hydroxylated MgO at various sites was considered; IR and EXAFS data agree well with geometric and vibrational parameters calculated theoretically at the density functional level. The Re–$O_{surface}$ bond energy, 3.5 eV, is markedly higher than that of the Re–CO bond, identifying the surface as a strong polydentate ligand. The rhenium carbonyls are bonded most strongly at corner sites.

Similarly, IR, EXAFS, and density functional theory indicate that $Rh(CO)_2$ bonds at a four-ring of the faujasite framework; the Rh center is bonded to two O centers near an Al center with a Rh–O distance of 2.2 Å. Only by using theory in combination with the experiment was it possible to discriminate among the candidate structural models that are consistent with experiment. The results help to clarify the strengths and limitations of EXAFS spectroscopy for characterization of surface structures.

The interactions of metal clusters, Ir_4 with zeolite X and of Os_4, Os_5, and Os_5C with various MgO(001) sites (including defects), were also investigated. Theory indicates metal–surface oxygen distances matching EXAFS values but metal–metal distances in the clusters that are about 0.2 Å less than the EXAFS values, consistent with the suggestion that the clusters were not ligand free (i.e., that their decarbonylation from the parent $[Ir_4CO)_{12}]$ or $[Os_5C(CO)_{14}]^{2-}$, respectively, did not proceed by simple removal of CO ligands).

The theoretical results show that the support does not induce significant charge transfer in the supported Ir_4 clusters; rather, it causes a moderate charge rearrangement in the bonding region between the metal and O centers, accompanied by a small polarization of the electron density. Thus, we suggest that small noble metal clusters on zeolite and metal oxide supports are nearly zerovalent and that some effects of supports in catalysis may be explained by the polarization.

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Cluster Ion Beam Deposition for Catalysis Studies

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Supported catalysts are important in many areas of interest to the Department of Energy, including combustion, emission control, fuel cells, and chemical synthesis and conversion. A large body of work has explored the effects of particle size on catalytic behavior, and significant size effects on activity, product branching, and catalyst lifetimes have been reported, both for real and planar model catalysts. These experiments typically have a distribution of particle sizes present, and for small particle sizes the distribution may obscure interesting behavior.

The focus of our research program is on studying planar model catalysts containing size-selected clusters, prepared by deposition of pre-formed, mass-selected cluster ions. We have developed a phase-space-compressed ion deposition beam line that is capable of depositing at energies down to ~1 eV -- low enough to avoid cluster dispersal for most systems. Deposition is also possible at up to keV energies, allowing production of embedded cluster catalysts. Clusters are produced in a 100 Hz laser vaporization source. The beamline is coupled to a UHV system with STM, XPS, TPD/TPR, and EELS capabilities, along with facilities for sample preparation. Initial experiments on deposition of copper and gold clusters will be presented.

Spatially Resolved Chemistry One by One

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Chemistry at solid surfaces is ubiquitous in nature and occurs in many technological processes. In our constant drive to optimize energy usage and to minimize the detrimental effects on the environment, a firm scientific understanding of surface chemistry is necessary. The degradation of materials, such as corrosion, and the inefficient use of energy, as in frictional dissipation, continue to tax our energy demands. Synthesis of novel materials and fabrication of devices consume energy and can benefit from a rational approach. The recently announced nanotechnology national initiative reaffirms the need to understand matter and its interactions with the surrounding at the atomic and molecular level. In effect, individual atoms and molecules are the basic building blocks of all materials and the fundamental constituents of all energy processes. The ability to control chemistry at the level of individual atoms and molecules underpins the way they interact and use the available energy to affect chemical transformation.

The scanning tunneling microscope (STM) is a tool which not only allows us literally to see individual atoms and molecules but also to manipulate and spectroscopically characterize them. It is an all-purpose tool and is in effect a nanoreactor carrying out reactions with atoms and molecules in the nanocavity of the tunnel junction. Since the coupling of electrons to the nuclear motions provides the driving force for chemical transformation, the STM with its tunneling electrons can be tuned to induce atomic motions. We have built variable, low temperature (8 K – 350 K) STMs in ultrahigh vacuum to probe chemistry at the spatial limit.

It is a well known fact that STM images are difficult to interpret. We have demonstrated that chemical analysis with the STM is possible with inelastic electron tunneling spectroscopy (IETS) and have reached the limit of sensitivity of vibrational spectroscopy, that of a single bond. The ability to measure spatially resolved vibrational modes in single molecules makes it possible to directly determine and measure quantitatively a number of fundamentally important chemical processes. These include intramolecular energy transfer, energy dissipation resulting from bond breaking, chemical identification and structural determination of reactants and products involved in the making of individual chemical bonds and intermediates in multistep reactions, and the elucidation of the coupling of electrons to nuclear motions via individual molecular orbitals. By controlling the energy and flux of tunneling electrons and the inherent sub-Ångström spatial resolution, the STM nanoreactor gives rise to energetically and spatially resolved chemistry on single molecules one by one. It is possible to identify and inject electrons into specific molecular orbitals which are involved in chemical transformations. Through the tunneling electrons, the ability to control energy with sub-Ångström spatial resolution offers a new window for viewing and understanding atoms and molecules and their transformations in nature.

Cluster Reactions: An Approach to Elucidating the Physical Basis of Heterogeneous Catalysis

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The overall objective of our program is to obtain a more complete understanding of the physical basis for catalysis with specific focus on elucidating the role of certain properties such as oxidation state, degree of aggregation, stoichiometry, and charged state, parameters which greatly influence catalytic behavior. It is expected that the knowledge gained will ultimately contribute to attaining the ability to design catalysts with a high degree of selectivity, and to the development of ones that will yield the facile formation of desired products. Major emphasis is being given to an investigation of oxides, carbides, and nitrides of various transition metals and in some cases certain alloys, with attention to unraveling the reaction mechanisms of several classes of small molecules which comprise important constituents of the effluent of combustion processes, and whose releases to the atmosphere are environmentally undesirable. Clusters provide valuable models of various heterogeneous surfaces, and in some cases are even the substrate media employed in the formation of catalytic materials. Moreover, they can be readily formed in the gas phase and studied in an unsupported state. Hence, it is possible to unravel the influence of the various physical parameters referred to above without interfering effects from a support.

A comprehensive investigation of the reactivity of anion and cation nickel oxide clusters with NO_2, NO, and N_2O has been completed. Several different reaction mechanisms are found to occur, with considerable differences noted between anions and cations. Structural information on the clusters has been derived from collision induced dissociation in conjunction with theoretical calculations, and insights have been gained into the processes responsible for O atoms, O_2, and metal oxide loss.

As a continuation of our studies of Met-Cars discovered in our laboratory , we have measured the ionization potentials of those to which various ligands are bound. Theoretical investigations have led to the suggestion that, depending on the nature of the bound ligands, there is a potential for a shift in the electron density that can be expected to influence the reactive character of the ligands, and hence enhance the ability of Met-Cars to function as catalytic materials. Findings for methane adsorption, and its influence on ionization potentials will be given. Growing interest in the prospects of producing new catalysts from cluster assembled materials comprised of oxides, carbides, and nitrides of transition metals has prompted us to investigate the mechanisms of dehydrogenation, formation and growth of various cluster systems involving these materials.

In another related phase of our work, we have studied alloy clusters, on obtaining a basic understanding of the nature of chemical reactions occurring in the presence of clusters having varying valance electrons. Recent findings of the formation of aluminum-nitrogen numbers of species through chemical reactions display the manner in which available frontier orbitals influence reactivity. Particularly interesting is evidence for composite Jellium stabilized clusters in the aluminum-carbon and nitride systems, which we will discuss. The observed resistance to the attack of these by oxygen is an indication of the importance of electronic structure and thus provides an avenue to identify species that might be suitable candidates for producing new cluster assembled nanoscale materials.

Partial Oxidation of Benzene and Higher Aromatics with N_2O over MCM-22

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Phenol is manufactured primarily via the multi-step cumene oxidation process. This process needs to be run at low conversions to keep the selectivity high and the economic feasibility depends on the marketability of the acetone by-product. A one-step oxidation of benzene to phenol has always been an attractive alternative but has not been available until the discovery by Ono et al. [1] that using nitrous oxide (N_2O) over an acid catalyst it is possible to form phenol directly from benzene with high selectivity. Various solid catalysts have been used with ZSM-5 proving to be the most promising. Conversions of about 25 % and selectivities greater than 95% have been reported for the partial oxidation of benzene with N_2O over ZSM-5. The reaction mechanism of benzene oxidation by N_2O is still a matter of controversy. The group lead by Panov [2] believe that the iron present (sometime present at impurity levels) activates N_2O giving rise to what is called alpha oxygen. Alpha oxygen then oxidizes benzene to phenol. Other researchers (Burch [3], Motz [4]) believe that it is the Bronsted acid sites or the coordinately unsaturated species (eg. extra-framework aluminum) that is responsible for the oxidation.

MCM-22 is a novel aluminosilicate which has a very unique structure. It has two independent pore systems. In addition to a 2 dimensional 10 member ring (MR) channel (0.5 nm) system, it also has a second independent channel system composed of 12 MR cage structures (0.71 nm diameter x 1.82 nm height) connected to each other through 10 MR windows. The crystals of MCM-22 are hexagonal with a thin flat plate-like morphology. The crystal exterior is composed of "cups" which are essentially the 12 MR cage structures cut into half. This unique structural feature of MCM-22 gives rise to external acid sites which have acid strengths comparable to the internal acid sites of other microporous aluminosilicate (such as ZSM-5) and which are accessible to organic molecules which do not fit through the channels.

We have investigated the partial oxidation of benzene over MCM-22 and we have found that it is very active for the partial oxidation of benzene to phenol using N_2O. The conversions obtained are nearly 15 % with selectivities greater than 95 %, while the rate of deactivation is slow. Here we present an investigation of the catalytic properties of MCM-22 for the direct oxidation of benzene using N_2O. We are investigating the reaction mechanism using Near Edge X-ray Absorption Fine Structure (NEXAFS) and we will present preliminary results that explore the use of N_2O for the oxidation of naphthalene and biphenyl.

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Structure/Property Relationship in Transition Metal Carbides and Nitrides

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Transition metal carbides (TMC) and nitrides (TMN), especially those of Groups 5-6 early transition metals, are characterized by many intriguing physical and chemical properties. For example, they often possess catalytic advantages over their parent metals in activity, selectivity and resistance to poisoning. It has been shown in the catalysis literature that TMC and TMN are promising catalytic materials in a variety of chemical reactions. One of the primary motivations for the catalytic studies of TMC and TMN is that they often show catalytic properties that are characteristic of the expensive Pt-Group metals (Pt, Pd, Ir, Rh, and Ru). Furthermore, TMC and TMN often show higher tolerance than the Pt-Group catalysts towards catalytic poisons such as sulfur and nitrogen. As a result, TMC and TMN can potentially be used as the less expensive and more poison-tolerant replacements for Pt-Group metals, which are among the most commonly used commercial catalysts in a variety of industrial applications.

Despite these existing and potential applications of TMC and TMN in a wide range of technologically important processes, systematic studies aimed at the fundamental understanding of the structure/property relationship of these compounds are relatively scarce. This is especially true regarding the intriguing chemical and catalytic properties of TMC and TMN of Groups 5-6 metals. Our overall objective of the proposed activities is to determine the fundamental relationship between the chemical properties of TMC/TMN and their underlying electronic and physical structures.

Model Microcrystalline Mixed-Metal Oxides for Partial Oxidation and Desulfurization

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Our work has focused on the investigation of important catalytic processes: NO_x reduction, selective hydrocarbon oxidation, and the reduction of NO in the presence of hydrocarbon radicals. We have specifically investigated the site selectivity in specific elementary steps. In a second phase of our work, we have studied the effects of structure on the reactivity of nanophase Co particles grown on Mo-based substrates. Surface science techniques are used to determine the oxygen coordination sites populated, the oxidation states present, and the structure of the surface as well as to identify reactive intermediates. The reaction of alkyl species with different types of oxygen on thin-film oxides of Mo have been studied to probe the C-O bond formation step in hydrocarbon oxidation. The thin films serve as model systems on which to investigate the oxidation processes. Specific types of oxygen coordination sites are populated on oxidized Mo(110) by controlling the oxygen flux and oxidation temperature. We have found that reaction with oxygen in high-coordination sites is kinetically most favorable for reaction with methyl radicals. We find no evidence for participation of the Mo=O sites in the C-O bond formation step. We do find that the presence of Mo=O sites effects the facility for complete dehydrogenation which is important in determining selectivity. We have generalized this result by studying other alkyl radicals and found that oxygen in high coordination sites is generally very reactive. In our studies of NO, we have found that formation of a dinitrosyl species, in which two NO molecules are bound to the same metal center, lead to a low-temperature pathway for NO reduction. The selectivity and efficiency of this process depend on the number of oxygen vacancies on the oxidized surface. The dinitrosyl species is also important in the combined oxidation of methyl radicals and reduction of NO. Methyl radicals directly abstract oxygen from molecular NO species at low temperature (100 K) and yield gaseous reduction products and adsorbed methoxy. This offers insight into a possible mechanism for this important reaction on oxides. In our studies of nanophase Co islands on Mo-based substrates, we find that surface strain can be used to form metastable structures of Co and to limit their size. In some cases, the reactivity of these islands is substantially different than for Co with a bulk-like structure. For example, a Co lattice with a large lattice constant, enforced by interaction with sulfur on the substrate below, is resistant to oxidation by O_2. In summary, our work has demonstrated that elementary steps in chemical processes important in catalysis often have a strong sensitivity to structure on an atomic scale.

The Effect Of Adsorbed Alkylidyne On The Dynamics Of Adsorption Of Methane On Pt(111)

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In general, adsorption is the first step in all heterogeneously catalyzed reactions, and in many cases it may be rate-limiting. The overall purpose of this research is to understand direct and precursor-mediated adsorption by coupling the tools of modern surface science with molecular beam techniques. The work reported here is a part of our effort to understand the dynamics of adsorption in reactive collisions on clean and adsorbate-covered surfaces. Bond activation in this manner is a critical step in many heterogeneously catalyzed reactions important in the energy field; the activation of CO in methanation on nickel, of alkanes in steam reforming, of N_2 in ammonia synthesis, of alkanes in selective oxydehydrogenation and catalytic combustion are but a few important examples.

Recently we have focused our attention on adsorption mediated by extrinsic precursor states. In heterogeneously catalyzed reactions surface coverages of reactants and intermediates may vary, and appreciable coverages may be reached under some conditions of temperature and pressure. For example, in the hydrogenation of ethylene on both supported and model platinum catalysts, the surface shows appreciable coverage by ethylidyne - which itself is not an intermediate in the reaction. Thus, it is clear that understanding adsorption on both clean and adsorbate-covered surfaces is important to catalysis. In this meeting we present the results of the influence of adsorbed alkylidyne intermediates on the adsorption dynamics of methane as a prototypical study. These experiments were facilitated by use of a crystal manipulator that allowed the surface to be resistively heated to 1200K or cooled to 30K using a liquid helium cryostat.

The dynamics of the trapping of methane onto p(2x2)-ethylidyne, -butylidyne, and -isobutylidyne overlayers on Pt(111) at 50K were investigated. Since each of these adsorbates forms the same structure, trapping dynamics could be studied as a function of the internal structure of adsorbate. Trapping probabilities on these surfaces at a fixed incident energy and angle increase in the order oxygen < ethylidyne < isobutylidyne < butylidyne, and each of the adsorbate-covered surfaces enhances trapping compared to the clean surface. On the butylidyne-covered surface the initial molecular trapping probability decreases from 0.88 to 0.38 as the incident energy is increased from 8 to 24 kJ/mol, compared to a decrease in trapping probability from 0.3 to zero over the same energy range on the clean surface. The angular dependence of the trapping probability indicates that the overlayers lead to an increase in the static corrugation in gas-surface potential. The generally higher values of the trapping probabilities on the alkylidyne-covered surfaces and the weaker angular dependence they exhibit suggest that they have a more corrugated potential when compared to the clean surface.

Morphological and Kinetic Aspects of Surface Processes

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This program is focused on the fundamental surface science of systems that are models for heterogeneous catalysis of hydrocarbons. Single crystal metals and metal particles on planar supports are studied using the tools of ultrahigh vacuum microscopy and spectroscopy, including scanning tunneling methods. Adsorbate species that are important catalytic intermediates are singled out for synthesis, for structural characterization and for kinetic characterization.

Extrinsic precursor-assisted synthesis of 1,5-hexadiene on Cu(100). As allyl bromide is being dosed, its reaction with previously chemisorbed η^3-allyl to form 1,5-hexadiene on Cu(100) at cryogenic temperatures has been examined using RAIRS. Above 110 K, the 1,5-hexadiene formation rate decreases with increasing temperature and is controlled by the residence time of dosed allyl bromide, whereas below 100 K, the rate increases with temperature and is controlled by the reaction of weakly adsorbed allyl bromide with chemisorbed η^3-allyl. Above 110 K, a precursor state model describes the kinetics. The activation energy difference, (E_d-E_r), between desorption and reaction of allyl bromide with η^3-allyl is 12 kJ/mol. This work provides direct evidence for an extrinsic precursor-assisted reaction to synthesize a stable product that is not chemically bonded to the metal substrate.

Stepwise dissociation of thermally activated phenol on Pt (111). The thermal reactions of phenol on Pt(111), including characterizations of reaction intermediates, have been studied between 125 and 1100 K by using isotopically labelled phenol. Phenol adsorbs molecularly at 125 K, with the ring plane parallel to the surface. During heating, the O–H bond breaks below 200 K. The O–H bond dissociation product, phenoxy, has a quinoidal structure with bonded through the C_2 through C_6 atoms with the C_1 atom tilted away from the ring plane. Bonds in the phenoxy species rearrange towards oxocyclohexadienyl upon heating. Below 0.5 ML, phenoxy fully decomposes upon heating to CO(g), H_2(g), and C(a). Above 0.7 ML coverags, 85 % forms CO(g), H_2(g), C_2(a), and C_3H_3(a) at 490 K, the latter dehydrogenating to H_2(g) and C(a) above 550 K; and 15 % forms C_6H_6(g) and O(a) between 380 and 530 K. Selective C_2–H and C_3–H dissociation occurs within phenoxy.

Time-of-flight TPD. A new method of thermal programmed desorption (TPD) using time-of-flight mass spectrometry (TOFMS) is developed for simultaneous detection, in wide mass ranges, of large molecules and their surface reaction products. It provides a 3D TPD spectrum that contains a complete set of conventional 2D TPD spectra of all the masses in the mass range of interest. A 3D TPD spectrum of (methylcyclopentadienyl)Ir(1,5-cyclooctadiene), of which molecular weight is 379.53 AMU, on a rhodium surface is presented as an example. The 3D TPD spectrum comprises TOF mass spectra, from 1 to 385 AMU, accumulating 10,000 scans in every 0.6 second. By covering the whole mass range of interest in one TPD experiment, the new TOFMS-TPD offers some advantages compared to conventional quadrupole-based TPD.

Morphological Instability in Model Thin Film Catalysts: Structure, Reactivity and Electronic Properties

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We are exploring interesting new aspects of the relation between microscopic surface structure and chemical reactivity for model bimetallic catalysts used in energy applications, i.e., ultrathin films of metals on metals. Our focus is on atomically rough, morphologically "unstable" single crystal surfaces that may undergo massive reconstruction and faceting at the nanometer scale when covered by ultrathin films of metals or other adsorbed species (~ 1 monolayer thick), upon annealing to elevated temperatures. We are extending our studies beyond the body centered cubic, bcc, W(111) and Mo(111) surfaces to the face centered cubic, fcc, Ir(210) surface, and to atomically-rough hexagonal close packed, hcp, Re surfaces.

The overall objectives of this work are:

- *to characterize, with atomic resolution, the nanometer-scale faceting of atomically rough transition metal surfaces (bcc W, Mo; fcc Ir; hcp Re) covered with ultrathin metal films,*
- *to correlate the surface structure and morphology with chemisorption and catalytic activity for faceted surfaces using structure sensitive catalytic reactions, and to search for special kinetic effects associated with nanometer scale surface features,*
- *to correlate faceting and reactivity with surface electronic properties and alloy formation, using high resolution synchrotron radiation measurements.*

We are using a variety of ultrahigh vacuum (UHV) surface science methods, including atomic resolution scanning tunneling microscopy (STM) and catalytic studies. A few recent highlights are: *First*, we have obtained the first atomically-resolved scanning tunneling microscope (STM) images of nanoscale {112} and {110} facets caused by faceting of annealed Pt- or Pd-covered W(111). *Second*, we have used UHV STM and Low energy electron microscopy (LEEM) to identify the nucleation and growth conditions for facet formation (collaboration with G. Kellogg, Sandia). *Third,* we have carried out extensive studies of the surface chemistry of C_2H_2 on planar and faceted Pd/W surfaces using high resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD); we find that ethylene formation and cyclotrimerization to benzene are highly sensitive to surface structure, as well as to facet size. *Fourth,* we have discovered that Pt, Pd and Rh cause an unusual reconstruction of W(112), and have characterized desorption kinetics and structure using LEED, TPD and STM. We have also used field emission microscopy (FEM) to characterize W(112) facet growth. *Fifth,* we have found a remarkable nanoscale (4 x 4) reconstruction of W(111) induced by adlayers of a catalytic modifier, sulfur. We are now characterizing the structure and reactivity of metallic films deposited onto the S (4 x 4) surface: Pt, Pd, Cu. *Sixth,* we have discovered that oxygen induces nanoscale faceting of Pd(210), and are beginning studies of overlayer metals. *Seventh*, we have studied many bimetallic systems using soft x-ray photoemission spectroscopy (SXPS) based on synchrotron radiation, and find that surface core level shifts (SCLS) are excellent diagnostics of interfacial properties; in an interesting series of experiments, conditions for surface alloy formation have been identified.

These activities have been enhanced by multiple collaborations, (J. -G. Chen, EXXON (now at the University of Delaware); J. E. Rowe, ARO-Durham and NC State University; G. Kellogg, Sandia National Laboratory; R. Blaszczszyn, Poland; C. -T. Chan, Hong Kong Univ. of Sci. and Technol.).

The factor that distinguishes this work from other studies of model bimetallic catalysts is our emphasis on atomically rough, high surface energy surfaces that may be morphologically unstable during reaction conditions. These atomically rough surfaces should be more accurate models for high area bimetallic catalysts, and ours are the first detailed microscopic studies of faceting induced by monolayer metal films. We believe these results are of importance in understanding dynamic structural rearrangements at the surfaces of high area bimetallic catalysts under high temperature operation, and in clarifying the role of nanometer-scale facets on size effects in surface reactions.

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Probing Surface Chemistry under Catalytic Conditions: Hydrogenation and Cyclization

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A palladium single crystal model catalyst is covered by a strongly bound carbonaceous layer during catalytic hydrocarbon conversion reactions. In the case of Pd(111), these layers are well defined and consist of vinylidene species during acetylene cyclotrimerization and ethylidyne species during ethylene hydrogenation. In ultrahigh vacuum, these carbonaceous layers are unreactive and also suppress subsequent adsorption onto the metal surface. Infrared spectroscopy experiments reveal that molecules, for example CO, can adsorb onto the metal surface at high pressures (several Torr). In addition, molecular beam methods can be used to probe adsorption onto these carbonaceous-layer covered surfaces and are used to measure isosteric enthalpies and entropies of adsorption of probe molecules, for example carbon monoxide. Moreover, these carbonaceous layers, although inert in ultrahigh vacuum, can react at higher pressures. For example, it is found that adsorbed vinylidene species on Pd(111) react with gas-phase acetylene to form benzene at the same rate as that at which benzene is formed catalytically from acetylene on that surface. In addition, ethylidyne species are removed from the surface by high pressures (several Torr) of gas-phase hydrogen in a reaction that is first-order in hydrogen pressure. Adsorbed vinylidene species react with hydrogen to form ethylidyne species that are then removed from the surface. The results suggest that the carbonaceous layers can play a central role in the catalytic reaction. They also reveal that, during hydrogenation catalysis, the nature of the surface can change with the reaction conditions (hydrocarbon and hydrogen pressures and temperature).

Partial Oxidation of Hydrocarbon:
Surface Science and Catalytic Studies

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The mechanistic details of hydrocarbon partial oxidation reactions are being studied by using both ultra-high vacuum (UHV) modern surface-sensitive techniques and micro-batch reactors. Partial oxidation processes are key building blocks for the design of more efficient ways to convert hydrocarbons from crude oil and other natural sources into useful chemicals. The focus of our work has been on the characterization of the reactivity of alkyl species (prepared by activation of alkyl halide precursors) and of alcohols on nickel single crystals and foil surfaces. The oxidation of 2-propyl iodide on oxygen-treated Ni(100) in particular was found to yield a number of products, including some from partial oxidation steps. XPS I 3d core level spectra indicate that the adsorption of 2-propyl iodide below 100 K is molecular, and ISS data strongly suggest preferential bonding to Ni sites. Annealing of adsorbed 2-propyl iodide moieties on O/Ni(100) surfaces between 120 to 200 K generates 2-propyl groups on the nickel sites (via dissociation of the C-I bond), the same as on the clean surface. In the case of submonolayer oxygen coverages, oxygen atoms then insert into the metal-carbon bond of nearby alkyl moieties to form 2-propoxide groups. The acetone desorption peak shapes and temperatures seen from thermal activation of 2-propyl iodide and 2-propanol on O/Ni(100) are nearly identical, suggesting that they form from a common intermediate, 2-propoxide; that species was identified directly in both cases by infrared spectroscopy. 2-Propoxide moieties are stable on the surface up to ~325 K, at which point they undergo a rate-limiting β-hydride elimination to yield acetone. Other TPD experiments indicated that propene does not react to yield acetone on O/Ni(100) surfaces; it is suggested that in catalytic systems that reactant may rather go through a previous hydrogenation step to alkyl intermediates before oxygen insertion and β-hydride elimination to the ketone.

Additional surface science experiments provided further insight into some of the parameters that affect the selectivity of the catalytic surfaces towards the partial oxidation pathway. For one, it was found that subsurface oxygen, the result of oxygen diffusion into the bulk after high temperature treatments, is still active towards acetone formation. Perhaps more interestingly, the presence of hydroxide groups on the surface also enhance the yield for ketone production in a significant way. In fact, even though similar β-hydride elimination steps from surface ethoxide may also lead to the production of acetaldehyde from ethyl groups, this process only takes place on the OH-covered substrate; no aldehydes desorb from surfaces treated with oxygen alone. Catalytic experiments indicated that alcohols can indeed be converted to aldehydes or ketones with high selectivity by using nickel surfaces under controlled conditions, a result that validates the knowledge obtained in the mechanistic studies. Kinetic parameters were obtained for these processes. We are presently extending our work to the characterization of oxidative coupling reactions, a promising route for the conversion of natural gas to other more valuable chemicals.

High Pressure Heterogeneous Catalysis in a UHV Environment: The Role of Bulk H

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A continuing goal of our group's research is to uncover the microscopic processes that give rise to differences between the surface chemistry observed under ultrahigh vacuum (UHV) laboratory experiments and that observed under high pressure, practical conditions of heterogeneous catalysis. Of particular concern is the apparent lack of reactivity of surface chemical reactions under UHV conditions. This goal is important, because the lack of reactivity under these conditions where surface sensitive techniques are operable casts doubt on the relevance of UHV surface science to industrial processes such as catalysis. This goal is also important because a molecular level understanding of the apparent unreactivity can be used to design schemes to effect these reactions under the low pressure, single collision conditions of a UHV experiment where the reactants and intermediates can be unambiguously identified. The discovery of new reaction mechanisms may ultimately lead to schemes for the development of novel catalytic processes.

The hydrogenation of ethylene on Ni(111) is a reaction that does not proceed under UHV conditions, although it readily takes place at high pressures. Recently, our laboratory discovered that H absorbed in the bulk of Ni metal is the reactive species in the hydrogenation of ethylene. Although bulk H is normally only present at high pressures, our laboratory demonstrated how to synthesize it under UHV conditions using molecular beam techniques and has also shown how to detect and spectroscopically characterize it by high resolution electron energy loss spectroscopy (HREELS). The inability to produce bulk H by exposure of most single crystal transition metals to an ambient gas of H_2 at low pressures precluded these reactions from being studied and therefore precluded the identification of bulk H as the reactive species in ethylene hydrogenation. In short, these investigations into the origin of the unreactivity under UHV conditions have resulted in the discovery of a new kind of surface reactant, bulk H, with a chemistry of its own.

We are presently investigating the interaction of H_2 with a Au-Ni alloy. The purpose of this investigation is to determine whether the presence of small amounts of Au on a Ni(111) surface changes the H-Ni interaction potential so as to make the dissolution of hydrogen into the bulk of the Ni thermodynamically favorable to remaining adsorbed on the surface and kinetically viable. If successful, this surface alloy may obviate the need for molecular beam techniques to simulate a high pressure condition of bulk H under UHV conditions, making these reactions accessible to investigation by the entire surface science community. The identification of the bulk H will by carried out by HREELS. As we have shown in our previous work, the bulk character of the hydrogen can be unequivocally determined from its dependence of the intensity of its vibrational loss feature on the energy of the incident electron. The results of these experiments will provide one general molecular level mechanism for the phenomenological changes in catalytic activity and selectivity that occur upon alloying.

Experimental, Structural, and Theoretical Studies of Active Oxygen Species for Catalytic Conversion of Hydrocarbons

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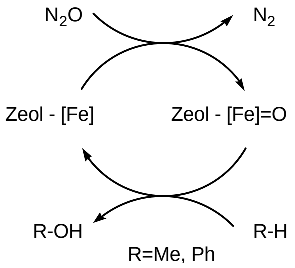
Catalysts enable energy technologies and affect energy savings, emissions reductions, and process efficiencies. One class of catalysts of broad current interest are redox-active catalysts for selective oxidation of hydrocarbons to value-added products and fuels. Many of these catalysts have site-isolated metal ions in zeolite hosts as active sites. Our recently initiated project strives to develop a fundamental understanding of the nature of site-isolated metal centers in zeolites that act as selective oxidation catalysts. Research in this area is required to develop more carbon-efficient processes to fuels that will enable the reduction of future CO_2 emissions. The catalyst systems we are interested in are closely related to a number of catalytic materials that promote the reduction of emissions from internal combustion engines.

We have a specific interest in the iron-containing zeolites that are known to mediate the hydroxylation of methane and benzene via formation of a putative iron-oxo intermediate. Because iron is dilute in these catalysts, the details of the local structure of these iron centers and how the structure promotes such unusual reactivity are not known at present. We are using both a molecular approach and a solid-state approach to understand the chemistry and structures of site-isolated metal centers.



We synthesize soluble, molecular compounds as analogs to the iron zeolites. We are in the early stages of employing a variety of techniques to extract information regarding the chemistry of such site-isolated iron centers. These approaches employ a combination of synchrotron and neutron techniques, theoretical techniques, nuclear magnetic resonance and other spectroscopies to obtain information on the iron zeolite catalyst, and are broadly applicable to other classes of site-isolated catalysts.

Our goals during the first year of this research include (1) the synthesis and catalytic testing of Fe zeolite materials to produce materials suitable for detailed structural investigations, (2) obtain neutron scattering and diffraction data for Fe-ZSM-5, particularly inelastic neutron spectroscopy (INS) on catalyst-bound protio- and perdeutero-phenol and methanol, and (3) explore the synthesis of molecular analogs to the iron zeolites.

To date, we focused on developing the chemistry of molecular iron silicates as analogs to Fe-ZSM-5. We successfully designed, synthesized, and characterized a number of novel polyhedral iron silsesquioxane complexes that represent potential models of iron sites in the zeolitic systems of interest, and obtained crystal structures of four of these iron silsesquioxane complexes. The chemistry, structures, and reactivity of these soluble iron silicates will be described.

Our future goals are to perform structural studies using neutron and synchrotron techniques on well-characterized samples. Isotopic labeling of the iron zeolites with stable isotopes will generate the iron pair distribution functions to complement data obtained using synchrotron techniques. Studies of the regiochemistry of insertion of the unique iron-oxo site into C-H bonds will develop additional understanding of the electronic features of the iron oxo species.

C-C and C-H Bond Activation of C3 through C6 Cycloalkanes on Ir(111)

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Advances in the research field of alkane activation and conversion would be enormously beneficial to the American economy, in general, and to the natural gas, petroleum, and chemical industries, in particular. Since alkanes are relatively inert, activation generally requires severe conditions such as high temperatures or very active substrates. However, controlled selective transformations will be disfavored, in general, by these conditions. The key appears to be finding catalytic systems that are capable of activating alkanes under increasingly more moderate conditions, and in quantifying the initial activation reaction. Discovering such catalytic systems are central to the Department of Energy missions in Basic Energy Sciences.

Towards this mission, the activation of cyclopropane, cyclobutane, cyclopentane, and cyclohexane on the hexagonally close-packed (hcp) Ir(111) surface has been measured for surface temperatures between 250 and 1000 K. Qualitatively, the activation data for these cycloalkanes are very similar since the Arrhenius plot for each reveals an activation energy change with temperature, indicating a shift in the controlling mechanism of the reaction. At low temperature ($T<400$ K), the initial dissociation step for these cycloalkanes occurs through cleavage of a C-H bond. As the surface temperature is increased above 400 K, the controlling mechanism shifts to C-C bond cleavage. Quantitative comparison of the experimentally determined C-C and C-H bond cleavage activation barriers reveals that the activation barriers of both mechanisms decrease with decreasing cycloalkane size. The lowering of the C-C bond activation energy with decreasing size is not surprising, considering that the inherent ring strain of these molecules increases with decreasing size. Therefore, the C-C bond activation data suggest that the ring strain effectively lowers the activation barrier for C-C bond cleavage. The decrease in C-H bond activation barrier with decreasing cycloalkane size is surprising, however, since the C-H bond in cycloalkanes becomes progressively stronger with decreasing molecular size. One explanation for the decrease in C-H bond activation barrier with decreasing cycloalkane size involves steric and geometric effects. Access to the cycloalkane C-H bond by the iridium *d* orbitals is sterically hindered in the larger cycloalkanes compared to the smaller ones. Also, because H adatoms behave somewhat differently on Ir(111) than on other surfaces (they are observed to adsorb in the terminal site even at moderate surface coverage on Ir(111)), it is possible that activation of sterically unhindered C-H bonds on this surface could be enhanced by a transition state for C-H bond cleavage involving a terminal-bonded Ir-H-C complex. These arguments provide a possible explanation for this observed C-H bond activation barrier trend based on geometric and steric arguments.

One set of future experiments involves measuring the activation of cycloalkanes on the hcp Ru(001) surface. These data, combined with cycloalkane activation data from Ir(111), will allow quantitative determination of the influence of electronic structure of the transition metal catalyst upon both C-H and C-C bond activation. Other areas of future experimental attention involve the reaction of various preadsorbed hydrocarbon overlayers on catalytic surfaces with gas-phase atomic hydrogen and gas-phase atomic oxygen with the hope of isolating new (and industrially relevant) surface intermediates.

Solid Base Catalysts Prepared by Occlusion of Alkali Metals and Metal Oxides in Zeolite Pores

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The current thrust to develop energy efficient, environmentally-benign chemical processes motivates research on solid acid and base catalysts as potential replacements for corrosive liquid catalysts. Compared to solid acids, the surface properties and reactivities of solid bases have been relatively unexplored. Incorporation of occluded alkali species in zeolite cages beyond the ion-exchange capacity creates new catalytically active base sites on the materials. However, the nature of the occluded alkali species has been elusive. In this work, the basicity and reactivity of alkali-modified zeolites were investigated in order to elucidate the role of occluded species on catalytic activity. To synthesize intrazeolite oxide or metal species, cesium acetate or cesium azide was impregnated into the pores of zeolites and decomposed *in situ*. Results from ESR spectroscopy, ion exchange and elemental analysis revealed that loading cesium (metal or oxide) into KX zeolite results in the formation of some occluded potassium (metal or oxide). The zeolite should be ion exchanged with cesium ions prior to impregnation of cesium azide or acetate precursors to prevent the formation of mixed phases. Differences in the Cs L_{III} edge spectra of zeolites loaded with cesium oxide compared to bulk cesium compounds indicated that cesium was more ionic in the supported samples. To characterize the basicity of the samples, adsorption of iodine and carbon dioxide was used. The blue shift in the visible spectrum of adsorbed iodine was found to increase with increasing electropositivity of the exchangeable cation, indicating greater donor strength of the zeolite framework. Since I_2 decomposed on samples containing occluded cesium oxide, CO_2 adsorption microcalorimetry was used to interrogate the stronger bases. The CO_2 uptake increased linearly with the amount of occluded Cs in X zeolite. A majority of the base sites in the CsO_x/CsX samples exhibited a heat of CO_2 adsorption around 85 kJ mol^{-1}, which is much lower than 270 kJ mol^{-1} seen on a commercial, bulk cesium oxide. After thermal pretreatment, Na(azide) and Cs(azide) modified X zeolites catalyzed the side chain alkylation of toluene with ethylene, whereas, CsO_x/CsX was inactive for the reaction. However, the catalytic activities of the CsO_x/CsX samples for the isomerization of 1-butene and dehydrogenation of 2-propanol increased linearly with the amount of excess cesium, which is consistent with the results from the adsorption microcalorimetry of CO_2.

Experimental and Theoretical Approaches for the Design of Catalysts Used to Produce Fuels and Chemicals

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The primary focus of this project is to develop an understanding of the fundamental structure-performance relationships for catalysts used to produce fuels and chemicals in a selective, energy-efficient manner. This objective is pursued through the use of both theoretical and experimental methods. The findings of this work are then used to guide the design catalysts that exhibit higher activity and selectivity for the formation of desired products. During the past two years, attention has been devoted to three primary themes: 1) molecular design of highly active catalysts for the synthesis of methanol; 2) elucidation of the reaction mechanism for the synthesis of dimethyl carbonate (DMC) and the structural requirements of the catalyst; 3) controlled oxidation of methane with the objective of forming methanol.

Our earlier work on the synthesis of methanol from CO and CO_2 over Cu/ZrO_2 demonstrated this catalyst operates in a bifunctional manner. CO or CO_2 react with Zr-OH groups on the surface of ZrO_2 to form HCOO or HCO_3 species, respectively. These intermediates then undergo stepwise hydrogenation on the ZrO_2 surface to form methanol. The dispersed Cu serves to adsorb H_2 dissociatively and provide H atoms to the ZrO_2 via spillover. Cu also promotes the reverse water-gas-shift reaction of CO_2. We have recently established that the surface properties of tetragonal and monoclinic zirconia are markedly different with respect to CO and CO_2 adsorption and the spillover of H atoms. The Zr-OH groups on monoclinic ZrO_2 exhibit higher acidity and basicity than those on tetragonal ZrO_2, and they are present in higher concentration. Likewise, spillover of H atoms occurs much more rapidly on monoclinic ZrO_2. Consistent with these observations, we have recently determined that the rate of methanol synthesis from both CO or CO_2 is more than an order of magnitude higher for Cu/m-ZrO_2 than Cu/t-ZrO_2. We are currently exploring the possbility of doping ZrO_2 with Mg and Zn cations to further alter the acid/base properties of ZrO_2.

The synthesis of dimethyl carbonate (DMC) from CO_2 and CH_3OH over ZrO_2 has been reported recently. We have investigated the elementary processes involved in this reaction using in situ Raman spectroscopy. Our findings show that CH_3OH adsorbs to form Zr-OCH_3 groups, which can then react with CO_2 to produce a precursor to DMC. Similar studies using in situ infrared spectroscopy have also been initiated. The objective of this work is to establish the surface properties of ZrO_2 required to achieve high activity and selectivity.

Our third effort is devoted to understanding how methane might be converted to methanol at trivalent metal cations located at cation-exchange positions in zeolites. Ab initio quantum chemical calculations have shown that N_2O will dissociate on $Al{=}O^+$, $Ga{=}O^+$, and $Fe{=}O^+$ cations to form peroxide anions. These anions will then react with CH_4 to form strongly bound $[M(OCH_3)(OH)]^+$ structures. The release of CH_3OH from these structures is energetically demanding but can be achieved by hydrolysis. We are currently exploring the details of the elementary processes leading to methanol through both experimental and theoretical approaches.

Experimental and Theoretical Studies of Surface Oxametallacycles: Connections to Olefin Epoxidation

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Improvements in the selectivity of oxidation of hydrocarbon feedstocks to chemicals and fuels directly impact both the efficiency of resource utilization and the reduction of greenhouse gas emissions. The focus of our research is on improving the performance of heterogeneous catalysts for selective olefin epoxidation and the development of new catalysis through increased understanding of surface reaction mechanisms and the influence of inorganic promoters on these. Relevant catalytic processes include the commercially practiced epoxidation of ethylene to ethylene oxide and the recently commercialized epoxidation of butadiene to epoxybutene (EpB), both carried out with silver catalysts, and emerging gold and silver catalysts for propylene epoxidation.

The guiding hypothesis of our research is that surface oxametallacycles are key intermediates in selective olefin epoxidation. By a combination of surface science experiments and Density Functional Theory (DFT) calculations, we have synthesized the first two stable surface oxametallacycles (on Ag(110)) and have verified their identities and structures. In the case of epoxybutene chemistry, we have been able to demonstrate direct connections between surface oxametallacycles and epoxide products. EpB ring opens with an activation energy of 8.4 kcal/mol on Ag(110) to form a stable surface oxametallacycle. Measured HREELS and NEXAFS spectra for this species are in excellent agreement with spectra calculated by DFT for an oxametallacycle bound to 3 silver atoms of a 7-atom cluster. This oxametallacycle undergoes 1,2- and 1,4-ring-closure reactions during TPD to form EpB and 2,5-dehydrofuran, respectively. This reaction represents the first demonstration of surface oxametallacycle ring-closure to form an epoxide, and we suggest that surface oxametallacycles are of general importance in silver catalyzed olefin epoxidation. Current efforts are investigating the influence of surface structure and of key catalyst promoters on this chemistry. By focusing on the newly commercialized epoxidation of butadiene, we have the opportunity to produce fundamental research that will have an impact early in the lifetime of the process. The development of oxametallacycle surface chemistry from this work promises to provide new understanding of olefin epoxidation, and potentially new processes for epoxide synthesis and derivatization.

Influence of Local Structure on Chemisorption Properties and Oxidation Reactions Over Metal Oxide Surfaces

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The research program is directed at understanding geometric and electronic structure/function relationships in metal oxide surface chemistry, with an emphasis on oxidation chemistry. Specific surface properties of interest are cation oxidation state, cation and anion coordination number, and any unusual properties associated with point defects, particularly surface oxygen vacancies. The work is aimed at improving our molecular level understanding of heterogeneous reactions in catalytic systems important in the production of fuels and chemicals. Work is currently being conducted on Cr_2O_3 $(10\underline{1}2)$ and SnO_2 (110) surfaces.

The presentation will focus on our recent efforts to characterize the chemical properties of surface oxide anions of different local coordination. Surface oxide ions are typically thought of as Lewis base sites [1,2] and our characterization efforts have centered on the use of acidic probe molecules. CO_2 is the usual probe molecule chosen to test the basicity of oxide surfaces. In the simple view of the acidic properties of CO_2, the addition of an oxide ion leads to the formation of surface carbonate, $CO_2 + O^{2-} \rightarrow CO_3^{2-}$. However, due to the different surface conformations adsorbed CO_2 may assume, CO_2 adsorption is a site specific, and is not a simple probe of the properties of surface oxide anions. The site-specific nature of CO_2 adsorption is demonstrated by studies on the Cr_2O_3 $(10\underline{1}2)$ surface. On the stoichiometric surface, five-coordinate cations with a single coordination vacancy are associated with a cation/anion site pair where CO_2 forms a bidentate surface carbonate (ΔH_{ads} = 24.8 kcal/mol). On the oxygen-terminated surface, terminal chromyl oxygen caps the single chromium coordination vacancy [3] and acts as an adsorption site for CO_2 (ΔH_{ads} = 14.5 kcal/mol).

BF_3, a strong Lewis acid, has also been used as an acidic probe molecule. XPS demonstrates that BF_3 bonds directly to surface oxide ions on Cr_2O_3 $(10\underline{1}2)$. In contrast to the results for CO_2 where the adsorbate conformations differ on the stoichiometric and oxygen-terminated surfaces, the measured heats of adsorption of BF_3 demonstrates that terminal chromyl oxygen is more basic than the three-coordinate oxide ions at the stoichiometric surface.

In addition to the experimental study, the results of a density functional study of the structural and electronic properties of stoichiometric and defective SnO_2 (110) surfaces will be presented. The predicted surface relaxations are in line with those reported previously by Manassidis *et al.*[4]. When the electron localization function (ELF) is used to examine the charge density for these surfaces, the polarization around surface cations and anions provides a picture of the relaxations that can be understood qualitatively in terms of a simple VSEPR model.

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Selective Oxidation of Hydrocarbons Over Mixed Metal Oxides: Spectroscopic and Kinetic Characterization of Sol Gel and Combinatorial Catalysts

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Mixed metal oxides based on V, Mo, and W are widely recognized as active and selective catalysts for the oxidation and ammoxidation of hydrocarbons. The most successful catalysts usually involve complex mixtures of oxides that exhibit solid solution behavior, provided that appropriate synthesis procedures are used. The goal of our research is to develop a more fundamental understanding of the activity and selectivity of mixed metal oxides by using advanced characterization and kinetic techniques and by using new approaches for catalyst synthesis and activity measurements. New routes to important chemical intermediates and fine chemicals are an important focus of this research effort.

Traditional methods of catalyst preparation for reducible mixed metal oxides involve formation of multiple phases. Research has established that generation of solid solutions having site isolation of the active oxygen is essential. New preparation techniques offer the potential for extending the compositional range of solid solutions, particularly for ternary (or greater) metal oxide systems. We are using two techniques – sol gel syntheses and reactive sputtering – to expand the solid solution chemistry of V, Mo, and W oxides and to include other transition elements, such as Re, Nb, etc. Characterization of these materials involves laser Raman, FT-IR, and NMR spectroscopies, as well as XRD, XPS, TPD, and electron microscopy. Recent success has been achieved using these techniques to characterize the formation of vanadia-based sol gels: laser Raman and ^{51}V NMR studies have revealed the mechanism of gel formation in the presence of peroxide precursors. MQMAS NMR techniques are being extended to include other quadrupole nuclei, such as ^{95}Mo, ^{187}Re, and ^{17}O. Similar success has been achieved in studies of catalysts prepared by reactive sputtering. Amorphous precursors deposited in combinatorial arrays can be analyzed rapidly using *in situ* laser Raman spectroscopy and laser-induced fluorescence to verify the catalytic activity of specific solid solutions. These studies are then used to guide sol gel preparations.

Mechanistic pathways for new routes to partial oxidation products are being investigated using these catalysts. We are interested in relatively low-temperature conversions (200–300^{o}C) of $\geq C_4$ hydrocarbons, such as the partial oxidation of 1,3-butadiene to cyclic compounds (furan, dihydrofurans, furanones, and epoxides). Catalytic conversion of this di-olefin is fundamentally different from that for paraffin and mono-olefin feeds because of the absence of allylic hydrogen and because of the anticipated dominance of electrophilic oxygen addition. Recently, we have prepared mixed metal oxides that catalyze these conversions, and we are now investigating the nature of the active oxygen using ^{18}O-labeling experiments and *in situ* transient spectroscopic methods. These experimental approaches have lead to new insights into the nature of the active surface-layer oxygen involved in the redox (Mars-van Krevelan) mechanism.

Thermodynamic and Kinetic Aspects of Solid Acidity

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Catalytic cracking of hydrocarbon feedstocks is the largest volume catalytic process in current industrial practice. Effective utilization of these precious feedstocks requires control of catalyst performance to optimize yields of particular hydrocarbon products, e.g., control of chain length, paraffin/olefin ratio, extent of branching, etc. Moreover, the optimal properties of the catalyst depend on the nature of the feed. Therefore, it is vital to understand the factors controlling catalyst performance to be able to produce appropriate solid acid materials for the effective conversion of hydrocarbon feedstocks to valuable fuels and chemical intermediates.

In our work funded by the Department of Energy, we have identified an effective catalytic probe reaction to study the performance of solid acids for hydrocarbon conversion. Specifically, we study the conversion of isobutane in the presence of controlled concentrations of olefins in the feed. The products of this conversion are n-butane, propane, isopentane, 1-butene, cis-2-butene, trans-2-butene, propene, and isopentene. The selectivity patterns displayed by these products allow us to extract rate constants for various β-scission-olgomerization steps, hydride transfer processes, and branching rearrangements.

In our recent work, we have studied the role of rare earth cations in Fluid Catalytic Cracking (FCC) catalysis. Kinetic studies were conducted using two different sets of Y-zeolite catalysts, with 0 and 3.68 wt% of Rare Earth Oxide (REO). These catalysts were either calcined or steamed prior to the kinetic experiments. Heat flow microcalorimetry with ammonia as adsorbate at 423 K was used to probe the acid sites of the samples. The results showed that stable catalyst activity could be achieve using feed consisting of low concentrations of isobutene (<100 ppm) and high concentrations of isobutane (> 20%). Also, it was found that the reaction should be carried out at temperatures between 523 and 573 K, to achieve sufficiently high activity and yet to avoid initiation reactions caused by protolysis of isobutane.

Detailed kinetic experiments were performed to evaluate the catalytic activity and selectivity of different catalysts as a function of temperature, initial isobutane concentration, and isobutene feed level. The catalysts used in these experiments contained 0 and 7.84 wt% of REO. The identification and quantification of the Brønsted and Lewis acid sites was done by infrared spectroscopy, using ammonia and pyridine as probe molecules. The kinetic experiments were conducted at temperatures of 523 and 573 K; and, for each temperature the composition of the feed consisted of 10% hydrogen with isobutane concentrations of 20 or 80% (helium was the balance). For each isobutane concentration, the experiments were carried out with 5 different isobutene concentrations: 50, 100, 200, 300 and 400 ppm. We have used the results from these measurements to construct a kinetic model for isobutane conversion, based on adsorption steps, branching isomerization, oligomerization/β-scission processes, and hydride transfer steps. The predictions of the kinetic model are in good agreement with the experimental observations and can represent the trends observed for the effect of the REO in the performance of the catalyst.

Kinetics of Methane Combustion on Palladium Foils

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Catalytic combustion of methane (natural gas) is a promising technology to replace conventional burners on gas-fired turbines for power generation since it lowers NO_X emissions. Methane is the "greener" of the fossil fuels because it has the highest hydrogen to carbon ratio of all hydrocarbons and thus will produce the highest amount of energy per CO_2 formed when burned. Palladium shows the highest turnover rate for methane combustion and is going to be the catalyst of choice on commercial applications. Our objective is to understand many of the issues on the combustion reaction on Pd catalysts. We are currently studying Pd extended surfaces (foils) as model catalysts to investigate reaction kinetics, structure sensitivity, and sample activation.

An UHV chamber equipped with AES, XPS, and TPD is connected to a high presssure reactor that can be pressurized up to 1.5 atm. The sample can be transferred directly from the UHV chamber to the reactor cell through a welded bellows transfer arm. The palladium catalysts are 0.1-mm thick polycrystalline foils with a surface area of approximately 0.8 cm^2. The methane oxidation reaction is carried out under lean conditions (16 Torr CH_4, 160 Torr O_2 and N_2 balance to 800 Torr) at 598 K in a batch reactor with a reaction time of 170 min.

The kinetic data obtained on the Pd foil are in agreement with previously reported data for Pd-supported catalysts. Turnover rates based on the total number of metal surface atoms were calculated assuming a Pd foil surface atom density equal to the average of the low index planes (1.27×10^{19} atoms m^{-2}). The turnover rate observed was 41×10^{-2} s^{-1}, which is higher than the rates observed for Pd/ZrO_2 (18×10^{-2} s^{-1}) and Pd black (5×10^{-2} s^{-1}) catalysts. No activation during reaction was observed. Foils pre-oxidized in O_2 showed the same rate as initially clean ones. The reaction dependence order to CH_4, O_2 and H_2O were, respectively, 0.7, 0.2 and –0.9, and these values agree with previous results in the literature (1st order in CH_4, 0th order in O_2 to and –1st order in H_2O). However, the activation energy of 126 kJ/mol is lower than on supported catalysts (about 150 kJ/mol).

XPS analysis showed that to achieve a steady activity for the Pd foil, impurities such as silica and phosphorous needed to be removed before it reached full activity. However, a 18-fold improvement in the turnover rate was obtained (738×10^{-2} s^{-1}) on a fully active foil after treatment under rich conditions (160 Torr CH_4, 16 Torr O_2 and N_2 balance to 800 Torr) at 598 K. The activation procedure consisted of carrying out the reaction under rich conditions for 20 min, being careful to avoid depletion of O_2 in the gas phase. After treatment under rich conditions the turnover rate steadily decreased in subsequent lean runs and reached the rate of 252×10^{-2} s^{-1} after 6 runs. A foil oxidation treatment with no methane present and following activation in the presence of 5, 10 or 15 Torr of H_2O at 598 K for 150 min showed that the presence of water caused the deactivation. No deactivation was noticed when only oxygen was present. The higher activity in this case is tentatively assigned to the formation of a porous structure with a higher specific surface area.

Restructuring of Heterogeneous Catalysts

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Supported catalysts represent the mainstay of the chemical processing industry. These catalysts undergo restructuring during use, often irreversibly altering their properties and performance. *Catalyst selectivity and activity is very important for the energy efficiency of these processes.* Factors that influence restructuring include high temperature treatment, gas atmosphere and support chemistry. Addition of promoters modifies the properties of the supported catalysts and is often critical to maintaining the performance of a supported catalyst. There is a paucity of fundamental information on the role of adsorbates, promoters and the support on metal restructuring, making the design and operation of these catalysts a ‘black art.’ An understanding of the structure of the noble metal particles, and the role of restructuring in the reaction is important to further development of improved industrial catalysts.

In this research program, we are studying structural changes during catalyst activation and under reaction conditions. Our initial work is focused on two application areas: selective hydrogenation of acetylene in ethylene mixtures and the catalytic combustion of methane. We have focused our work on supported Pd catalysts. For the selective hydrogenation reaction, we have prepared a series of Pd catalysts on model SiO_2 micro-sphere supports. The catalysts were subjected to oxidation and reduction to vary surface structure. By performing the reaction under conditions similar to those in industrial practice, we have been able to elucidate some of the factors that are important to achieving improved performance in these catalysts.

The second major effort is on Pd combustion catalysts. These catalysts are used at temperatures where the phase transformation of PdO → Pd occurs, leading to hysteresis in catalyst activity. We have performed a careful study of the Pd←→PdO phase transformations under conditions relevant to methane oxidation. The results shed light on the complex reactivity behavior of Pd catalysts during methane oxidation.

This research program represents a partnership with The Dow Chemical Company under the DOE-PAIR (Partnership for Academic Industrial Research) program.

Applications of Palladium Catalysts In Energy Production Processes

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Fossil fuel combustion is the foundation of our modern industrial society; unfortunately, it is also the primary cause of anthropogenic air pollution and a major source of water and soil pollution. The simple solution to this problem - shutting the burners off - is not viable since it would result in dramatic declines in standards of living. Therefore emphasis is placed instead on combustion system modifications to produce inherently clean burners, fuel substitution, and exhaust clean-up devices. Implementing these solutions requires a detailed understanding of the chemical and physical mechanisms whereby pollutants are formed in flames and released to the environment, and relative rankings of the threats posed by different pollutants.

Our area of interest has been focused in the last years in two major directions: optimizing the catalytic performances of palladium based catalysts for “three way” applications, and to study the behavior of palladium based catalysts in the methane combustion reaction.

In a series of Temperature Programmed Desorption experiments we focused on the $PdO\text{-}CeO_2/\gamma\text{-}Al_2O_3$ system and $CeO_2/\gamma\text{-}Al_2O_3$ and $PdO/\gamma\text{-}Al_2O_3$ as references. The catalysts were prepared by different methods (co-impregnation, co-grafting and successive impregnation). For the $PdO\text{-}CeO_2/\gamma\text{-}Al_2O_3$ system, metallic palladium is important for NO reduction to N_2. Catalysts with equivalent Pd loadings and Pd particle size behaved differently with respect to NO and N_2 selectivity. The ceria-palladium interface correlated with high N_2 selectivity suggesting this is an important area for future study. The interaction between metallic palladium and reduced ceria was shown to favor the formation of N_2O, which may be the reason of the poor deNOx activity of palladium.

Our research also focused on the characterization of the state of palladium particles (HR-TEM, DTA-TG, UV-Vis DRS, TPR) following different thermal and chemical treatments in order to understand the modifications of the catalytic activity produced by variation of the reaction temperature on heating - cooling cycles or reaction mixture composition that may occur in automotive applications and in industrial gas turbines. We have shown that Pd has an interesting inhibition to reoxidize when cooled after complete thermal reduction. Activity excursions are also noted after partial reduction of the surface.

Recent pulse reaction test results were used to demonstrate how reduction strategy and degree affects reactivity. The degree of chemical reduction is temperature dependent. At low temperature only a surface layer of the PdO particles was reduced, while at high temperatures several subsurface layers are reduced. Following chemical reduction, activity increased dramatically and then rapidly decreased to 0 and started increasing again at different rates, depending on the temperature. At low temperature the catalyst activity stabilized at its initial value after a relatively low number of reaction mixture pulses, while at high temperatures remained considerably lower. By contrast, thermally reduced PdO particles showed an initial passivation against reoxidation and low combustion activity. They were observed to reoxidize at a very low rate and at a much lower temperature that the one observed under a constant oxygen partial pressure. This behavior was shown to be affected by the support.

Alteration of Selectivity and Activity in Hydrogenation Reactions

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Our program represents a study of the alteration and control of both selectivity and activity by MSI (Metal-Support Interactions) during the catalytic hydrogenation of complex organic molecules which represent generic reactions that are utilized in the fine chemicals and pharmaceuticals industry. Control of intramolecular selectivity to enhance the formation of valuable intermediate compounds can decrease the large amounts of waste byproducts now produced using non-catalytic methods (ca. 50-100 kg waste/kg product) which create environmental pollution problems. The use of heterogeneous catalysts to improve activity and (especially) selectivity also results in processes that are more energy efficient.

We are conducting this investigation via three approaches. 1) A careful kinetic study is underway of liquid-phase citral (a terpene, $C_{10}H_{16}O$) hydrogenation under conditions proven free of heat and mass transfer limitations in a state-of-the-art semibatch autoclave reactor. The kinetics to form intermediate products, such as the desirable unsaturated alcohol isomers via selective hydrogenation of the conjugated carbonyl bond, are being obtained to model a complex reaction network. Effects of the support and the solvent can be determined, and we have found that a TiO_2 support increases both the turnover frequency and selectivity to the unsaturated alcohol on Pt compared to conventional Pt/SiO_2 catalysts. Good liquid-phase kinetic studies are nearly nonexistent, thus the need of these studies. 2) An investigation of vapor-phase acetic acid hydrogenation is also ongoing using Fe and Pt Fe catalysts to determine the influence of support and the phase of Fe responsible for the high, desirable selectivity to acetaldehyde (80%). In contrast, Pt/TiO_2 gives selectivities of 60-70% ethanol and 20-30% ethylacetate whereas Pt/SiO_2 produces only CO and CH_4. In both of these studies, in situ DRIFTS, TPD and TPR are being employed to characterize the surface species, and Mössbauer spectroscopy is being used with the Fe catalysts. Chemisorption, XRD and TEM are also used to characterize the catalyst itself. 3) Finally, a UHV system utilizing AES, XPS, TPD and HREELS is being used to study crotonaldehyde (another organic molecule with conjugated -C=C-C=O bonds) adsorbed on a clean Pt surface as well as surfaces partially covered with TiO_x species. This program has previously shown that TiO_2 markedly enhances the hydrogenation rate to crotyl alcohol, and this study is determining the changes that occur in the adsorbed state due to the presence of TiO_x.

All these efforts are focused on a better understanding of the catalytic chemistry associated with the preferable activation of C=O bonds for hydrogen compared to C=C double bonds. During the past 3 years, the following results have been obtained that should benefit scientists working with liquid-phase reactions. 1) The reaction temperature can alter selectivity as much as the addition of a second metal. 2) Concurrent side reactions, such as decomposition to produce CO, can significantly inhibit the hydrogenation reactions, but the influence is very temperature-dependent. 3) MSI can increase the relative hydrogenation rate of the cis/trans citral isomers from 1.5 on Pt/SiO_2 to about 4 on Pt/TiO_2, thus providing unique separation opportunities.

Activity and Selectivity of a Pd/γ-Al_2O_3 Catalytic Membrane in the Partial Hydrogenation of Acetylene.

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The selective hydrogenation of acetylene to ethylene is a very important industrial process for the polymer industry (see reactions 1 and 2).

$C_2H_2 + H_2 \rightarrow C_2H_4$ Reaction 1

$C_2H_4 + H_2 \rightarrow C_2H_6$ Reaction 2

Acetylene is a contaminant in ethylene feed stocks for polyethylene production that causes numerous problems. Typically, the amount of acetylene in an industrial feed is about 0.35 wt %. Industry would like to reduce this concentration to 5 ppm. There are a variety of strategies to solve this problem, all of which require energy. Acetylene may either be separated out or reacted to ethylene without forming ethane. The latter is the most preferable in reducing costs. The idea is to selectively promote conversion of acetylene in reaction 1 and inhibit the formation of ethane from reaction 2.

The typical industrial catalysts have a low surface area with low metal loading, such Pd supported on α-Al_2O_3 . The metal loading is thought to be related to the dispersion of the metal and determine whether ethylene may readsorb for further reaction. The activity of the catalyst could be greatly improved by using a higher surface area support such as γ-Al_2O_3 with yet a still small metal loading. This increase in activity is often associated with a decrease in selectivity. However, a recent study by Lambert et al.[1] using a sol-gel Pd supported on γ-Al_2O_3 (BET area 334 m2/g, 3.6 nm pore diameter, 0.31 mL/g of pore volume, 0.8% Pd, 32% metal dispersion as measured by hydrogen chemisorption, and mean particle diameter of 3.1 nm) as a membrane reactor has shown increased selectivity. If the factors contributing to this increased selectivity can be understood, then industry would benefit.

Our catalytic membrane is supported on an α-Al_2O_3 tube (Membralox). Membranes are usually either ceramic or metal. Our ceramic tube has several advantages. There is little pressure drop across the membrane and no loss of catalyst. Ceramic supports are able to withstand increased temperature without embrittlement and offer higher permeability than metal membranes.

Typically, partial hydrogenation reactions carried out on catalytic membranes flow hydrogen through the shell side and the olefin though the tube side. The diffusion of hydrogen through the shell controls the selectivity. In our system, the best results occurred by premixing the two reactants and feeding both into the tube and out the shell (a conversion of 99.5% at 250°C and selectivity of 89.5% at 300°C, at a total flow of 18 mL/min, 50% Argon, 8:1 hydrogen to acetylene) [2]. This creates a flow distribution and different rates of permeation. This process was modeled using a one parameter dispersion equation for hydrogen, acetylene and ethylene and Dankwert's boundary conditions [3]. The reaction kinetics were assumed to follow a

Langmuir—Hinshelwood mechanism that was determined previously for a Pd/α-Al_2O_3 catalyst [4-5].

The computational results show that there was a definite change in either the kinetics or the transport mechanism at 175°C [1]. This may be the result of mass transfer limitations in the catalyst or the separative affect of the membrane or the permeation rate distribution of the reactants. A new rate law for our catalyst will clarify the kinetic contribution and further modeling of the dispersion reaction should determine the utility of the catalytic membrane in this application.

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Manipulation of the Catalytic Properties of Metal Particles

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In an attempt to optimize the efficiency of supported metal particles and the selectivity towards the formation of desired products we have mounted a fundamental program designed to explore the use of novel supports and unconventional reactor protocol in which only the catalyst is heated. This latter protocol has been found to not only reduce the energy required to carry out a given reaction, but also overcomes the problems associated with the uncatalyzed formation of carbon residues that normally accumulate on heated reactor walls.

The debate as to whether an "electronic" effect is responsible for perturbations in the normal behavior of supported metal catalysts has seized the attention of scientists for many years. Unfortunately, many of the proposed so-called "electronic" models can now be more satisfactorily explained in terms of either the surface concentration or the size of the ensembles present on the support surface. In this study we have used selected ceramic supports, including ferroelectric materials to demonstrate that at specific temperatures the catalytic activity of a supported metal particle can be enhanced to a significant degree. Ferroelectrics are materials that exhibit electrical polarization in the absence of an applied electric field. These solids possess a macroscopic electric polarization that is dependent upon the electric field. Such ceramics have a high relative dielectric constant (relative polarizability), examples include barium titanate and lead zirconium titanate. An important feature of these solids is that the permittivity can be altered by either stress (piezoelectrics) or temperature.

Mechanism Of Oxygen Storage By Nano-Particle Ceria

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Nano-particles of ceria, CeO_2, are widely used as catalyst support in automotive emission control systems. Their role is to maintain local oxygen pressure for precious metal catalyst by storing and releasing oxygen as the fuel-to-air ratio fluctuates. However, their relatively short life-time presents a major problem. In order to solve this problem the mechanism of oxygen storage has to be understood. Through the temperature- programmed-reduction (TPR) studies the presence of “active” oxygen, different from regular lattice oxygen, has been established. By using pulsed neutron scattering with the Rietveld refinement and the atomic pair-density function (PDF) technique, we identified the active oxygen to be interstitial oxygen defects. The interstitial defects are coupled with vacancies in the regular oxygen sites, forming so-called Frenkel defects. The total amount of oxygen (interstitial defects and regular sites) does not exceed the nominal stoichiometric value. The structure of ceria, fluorite structure, has a face-centered-cubic array of cerium ions, with the tetrahedral sites (regular sites) occupied by oxygen ions. The f.c.c. structure, however, also has octahedral interstitial sites which actually are larger in size than the tetrahedral sites. Apparently when reduced ceria is re-oxidized at low temperatures oxygen ions enter the meta-stable octahedral interstitial sites rather than the more stable tetrahedral sites. We conjecture that since these octahedral oxygen defects are more easily released they provide the low temperature oxygen storage capacity to ceria. The octahedral oxygen defects are abundantly found in nano-particle ceria, but after annealing they recombine with vacancies and disappear. Thus the kinetics of recombination and regeneration of the defects is the key in determining the effectiveness of the ceria catalyst support. It has been known that mixing with zirconia, ZrO_2, substantially prolongs the life-time of ceria. Indeed the octahedral oxygen defects are much more stable in ceria-zirconia mixture. Furthermore the TPR results of ceria and ceria/zirconia agree with the change in the density of oxygen defects with temperature. In addition the microstructure of ceria/zirconia mixture at nano-scale was found to be important for the performance. Nano-scale weak segregation of ceria-rich and ceria-poor domains appears to enhance oxygen diffusion. The research at present focuses on how to maintain oxygen defects regeneration capacity.

NOx Reduction under Oxidizing Conditions over Al_2O_3-supported Catalysts

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NO_x abatement under an oxidizing atmosphere, (often called lean NO_x abatement), has been a subject of intense research interest in the past decade. In part, this is due to the scientific excitement generated by the discovery of the highly active, zeolite-based catalysts, especially Cu-ZSM-5, both for NO decomposition and hydrocarbon reduction, and also the need for an effective exhaust treatment catalyst for lean-burn combustion engines. However, in spite of the huge volume of research concentrated mostly on studying and improving zeolite-based catalysts, no practical catalysts have been developed. The major obstacle to commercialization is insufficient long term stability.

Alumina is a commonly used support for many industrial catalysts. It is stable at high temperatures, and may make satisfactory catalysts for NO_x reduction by hydrocarbons. We hypothesized that there is no unusual active site requirements that can be found only in an environment provided by the ZSM-5 framework. Instead, the primary (but not the only) function of the zeolite framework is to stabilize the dispersed ion-exchanged cations from extensive agglomeration, a task that ZSM-5 does well because of the low Al concentration. Based on this hypothesis, we synthesized highly dispersed CuO_x in ZrO_2 as an effective NO_x reduction catalyst. Then, we proceeded to study the effect of dispersion of the supported active phase in $AgO_x/\gamma\text{-}Al_2O_3$ [1], $CoO_x/\gamma\text{-}Al_2O_3$ [2,3], $Au/\gamma\text{-}Al_2O_3$ [4], and, most recently, $SnO_x/\gamma\text{-}Al_2O_3$ catalysts [3,6]

It was found that the dispersion of the supported oxide or metal has a significant effect on the effectiveness of the catalysts to promote the hydrocarbon reduction of NO_x instead of combustion of hydrocarbon by O_2. This was observed on all four series of alumina-supported catalysts studied: $AgO_x/\gamma\text{-}Al_2O_3$, $CoO_x/\gamma\text{-}Al_2O_3$, $Au/\gamma\text{-}Al_2O_3$, and $SnO_x/\gamma\text{-}Al_2O_3$. For example, on the $CoO_x/\gamma\text{-}Al_2O_3$ catalyst, the dispersion of Co oxide depended on the loading and the calcination temperature. The Co oxide in a 2 wt.% Co/ $\gamma\text{-}Al_2O_3$ was highly dispersed, and no Co_3O_4 crystallites could be detected by either X-ray diffraction (XRD) or UV-vis diffuse reflectance spectroscopy (DRS). The Co ions on this sample were very resistant to reduction by H_2 up to 800°C. This catalyst was quite effective in NO_x reduction, and its properties were quite insensitive to the calcination temperature, up to 800°C. On the other hand, a 5 wt.% $Co/\gamma\text{-}Al_2O_3$ catalyst calcined at 550°C was a much less effective catalyst, and some of the Co ions in this sample could be reduced by H_2 below 800°C. Crystallites of Co_3O_4 could be detected on this sample by XRD and DRS. The Co_3O_4 crystallites could be dispersed by high temperature calcination to 800°C, and the dispersed Co ions became much more difficult to be reduced. Concurrently, the effectiveness of the sample for NO_x reduction also increases. A similar change in the NO_x conversion ability of metal ions and their reduction properties by H_2 was observed with $Cu\text{-}ZrO_2$ and $Ag/\gamma\text{-}Al_2O_3$.

For $SnO_x/\gamma\text{-}Al_2O_3$ catalysts, however, it was found that the specific activity increased with Sn loading (from 1 to 5 wt.% Sn), and the effective promotion of NO_x reduction over hydrocarbon combustion was obtained over a rather wide range of Sn loading (from 1 to 10 wt. %). The high activities were maintained even in the presence of 15% O_2 and 10% H_2O. The H_2-TPR profile of these samples showed, in agreement with XRD data, that at the lower Sn loadings, SnO_x existed as an amorphous phase that could be reduced quite easily. At the higher loadings, crystalline SnO_2 appeared, the reduction of which was slow, probably because of the low surface area.

An interesting observation is that, with AgO_x/γ-Al_2O_3, CoO_x/γ-Al_2O_3, and SnO_x/γ-Al_2O_3 under certain reaction conditions, a physical mixture of a catalyst with an otherwise relatively inactive oxide can generate a substantially higher N_2 yield than the catalyst itself. For SnO_x/γ-Al_2O_3, the enhancement was maintained even when the catalyst and the γ-Al_2O_3 were separated, provided that the SnO_x/γ-Al_2O_3 powder was upstream of γ-Al_2O_3. We have found further that oxygen-containing hydrocarbons are produced from SnO_2, which then reduces NO_x to N_2 over Al_2O_3. Thus, the SnO_x/γ-Al_2O_3 catalyst is a bifunctional catalyst.

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Plasma-Assisted Catalytic Reduction of NO_x

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Engine and automobile companies are placing greater emphasis on the diesel engine because of its potential for conserving energy resources and reducing CO_2 emissions. The modern diesel engine offers demonstrated fuel economy advantages unmatched by any other commercially-viable engine. The main drawback of diesel engines is exhaust emissions. Diesel engines operate under net oxidizing conditions, thus rendering conventional catalytic converters ineffective for controlling the NO_x emission. In the field of catalysis, one application that has been classified as a breakthrough technology is the catalytic reduction of NO_x in oxygen-rich environments using hydrocarbons. This breakthrough will require dramatic improvements in both catalyst and engine technology, but the benefits will be substantial for energy efficiency and a cleaner environment. The goals of this BES project are to (1) explore the effects of a plasma on the NO_x reduction activity, temperature operating window and durability of various catalytic materials, and (2) develop a fundamental mechanistic understanding of the interaction between the gaseous-phase plasma chemistry and the heterogeneous-phase chemistry on catalyst surfaces.

Plasma-assisted catalysis takes advantage of the selective partial oxidation of NO to NO_2 in a plasma to improve the NO_x reduction efficiency and durability of certain types of catalysts. NO_2 plays an important role in NO_x emissions control catalyst technologies. In selective catalytic reduction with hydrocarbons (a.k.a. lean-NO_x catalysis), many studies suggest that the conversion of NO to NO_2 is an important intermediate step in the reduction of NO_x to N_2. In lean-NO_x traps, the catalytic oxidation of NO to NO_2 on precious metals is followed by the formation of a nitrate on alkali or alkaline earth metal oxides. These technologies require low sulfur fuel because the catalyst component that is active in converting NO to NO_2 is also active in converting SO_2 to SO_3; the SO_3 leads to the formation of sulfuric acid and sulfates that increase the particulates in the exhaust and/or poison the active sites on the catalyst.

There is a heated debate over the need to reduce sulfur in the fuel so that catalyst technologies can efficiently reduce emissions of NO_x and particulates. The reduction of sulfur in the fuel will cost oil refineries billions of dollars. Low levels of sulfur will provide marginally acceptable durability for the catalyst technologies, but it is clear that the best NO_x removal efficiencies can be sustained only with zero sulfur. As environmental regulations get even tougher in the future, the need for alternative sulfur-tolerant technologies will emerge. The sulfur tolerance of catalyst technologies can be substantially improved by using a non-thermal plasma. The plasma can oxidize NO to NO_2 without oxidizing SO_2 to SO_3. Plasma-assisted catalysis can therefore reduce NO_x without requiring low-sulfur fuel and requires no or substantially less precious metals. The use of a plasma not only improves the sulfur tolerance but also increases the NO_x reduction efficiency of certain types of catalysts over a wider temperature range.

This presentation will report on our progress in understanding the fundamental mechanisms in plasma-assisted catalysis and demonstrate the effectiveness of the process for various catalyst materials.

Studies of Metal-Oxide and Oxide-Oxide Interactions in Automotive Emissions-Control Catalysis

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Improved, sulfur-tolerant, three-way automotive catalysts could enable the development of more fuel-efficient engines and limit constraints placed on sulfur in fuels. Ceria is a crucial component in these catalysts for providing oxygen storage (OSC) and it is this component that is sensitive to sulfur and to problems with aging. Our work investigates the mechanisms by which ceria plays its role and the changes that occur during deactivation.

We have demonstrated that the active form of ceria has weakly bound oxygen that does not exist on ceria after high-temperature treatment. This active form of oxygen can be observed in TPD studies on ceria films [1] and is responsible for high CO oxidation rates at low temperatures [2]. Pulsed-reactor studies show that reduced Pd/ceria can be oxidized by CO_2 and water [3], so that ceria-supported metals catalyze the water-gas-shift [4], steam-reforming [5], and CO_2-reforming [3] reactions by a redox mechanism in which a reductant on the metal reacts with oxygen from ceria. Ceria films supported on zirconia contain more weakly bound oxygen and are more active catalysts, probably due to the structure-directing nature of zirconia. For example, TEM shows that ceria films on a YSZ(100) crystal form epitaxial layers over the YSZ, with ceria having its normal lattice spacing [6].

Low levels of SO_2 (10 ppm) have no effect on precious metals, but significantly poison ceria. Surprisingly, amount of oxygen that can be stored in the catalyst, as measured by CO-O_2 pulse measurements, increases with the addition of ceria, so that this is not a good measure of OSC. By contrast, this level of SO_2 destroys the water-gas-shift activity, suggesting that the promotion of these reactions is most crucial. Spectroscopic studies to understand the role of sulfur are underway.

Finally, other reducible oxides, such as praeseodymia, have been examined as possible replacements for ceria and suggest reasons why ceria provides unique properties [7].

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The Selective Catalytic Reduction of NO by Propylene Over Supported Platinum Catalysts

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The selective catalytic reduction (SCR) of nitric oxide (NO) by hydrocarbons has received a lot of attention over the last few years because of its potential use in the control of NO_x emissions from lean-burn and Diesel vehicles. Such vehicles operate at high air to fuel ratios, which results in better fuel utilization. Noble-metal-based catalysts are the most promising candidates for this reaction due to their hydrothermal stability and low-temperature activity.

We have been investigating the selective catalytic reduction of nitric oxide by propylene (C_3H_6), in the presence of excess oxygen, over a series of platinum catalysts utilizing alumina and silica as the supports**.** Detailed kinetic and in situ FTIR spectroscopy studies were conducted in an attempt to understand the fundamental surface chemistry taking place during the SCR reaction. The Pt/Al_2O_3 and Pt/SiO_2 catalysts exhibit similar kinetic behavior indicating that the reaction proceeds through a similar mechanism on both catalysts. The results further indicate the presence of two kinetically distinct regions below and above the temperature of maximum NO conversion, as a result of the two competing reactions of propylene with NO and oxygen. In particular, the reaction was found to be zero order in NO at temperatures below that of maximum NO conversion, and first order in NO at temperatures above the maximum. Oxygen plays a dual role as a promoter at low temperatures and low oxygen concentrations, and as an inhibitor at higher temperatures and higher oxygen concentrations. The kinetic results suggest that the nature of the rate determining step is changing with temperature. The activation of propylene by molecular oxygen is believed to be the rate determining step at low temperatures, whereas the reaction of the activated hydrocarbon with NO becomes critical at higher temperatures. The presence of water did not affect the reaction rate significantly.

In situ Fourier transform infrared (FTIR) studies conducted under reaction conditions over the Pt/SiO_2 catalyst indicate the formation of a surface cyanide (-CN) species, and a gas phase/weakly adsorbed nitrous oxide (N_2O) species. The surface cyanide is the product of the reaction between an oxygen-activated hydrocarbon derivative and NO, and is reactive towards NO, NO_2 and O_2, resulting in the formation of N_2 and N_2O and CO_2. Its behavior, as observed in this study, is consistent with a role as a potential reaction intermediate. Similar FTIR studies over the Pt/Al_2O_3 catalyst revealed the presence of surface cyanide and isocyanate species. The reaction between NO and C_3H_6 in the absence of O_2 also produced the cyanide, but not the isocyanate. The surface cyanide in the case of Pt/Al_2O_3 is not a reactive intermediate. This species is very strongly adsorbed on the catalyst surface and does not react with O_2, NO, and NO_2. On the contrary, the surface isocyanate species is a potential reaction intermediate. This species is present only under SCR conditions (i.e. it is not present in the absence of O_2), is held weakly on the catalyst surface, and reacts with O_2, NO and NO_2. Based on the results of the kinetic and spectroscopic studies a reaction mechanism was proposed and was validated through micro-kinetic simulations.

Effect of Support Oxidation State Upon Chemisorption and Reaction at Rh/Ceria Model Catalysts

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We have studied the chemisorption and thermal evolution of various adsorbates on model catalytic surfaces composed of Rh supported upon highly oriented cerium oxide films. Our principal research focus has been on how the chemistry depends upon the degree of oxidation of the reducible support. First we find that the activity of ceria toward most adsorbates is strongly altered by the degree of reduction. Second, the surface activity of the metal particles is also altered by the extent of reduction of the support. These two factors combine to induce fascinating interactions that control the activity and reaction pathways of the composite system especially during redox reactions in which the extent of oxidation of the support may vary. A detailed understanding of such a model system may clarify the behavior of many catalyst systems for emission control in combustion devices, for example NO/CO conversion and selective reduction of NO under oxidizing conditions.

Cerium oxide films are grown on a Ru(0001) substrate and the extent of oxidation is controlled during growth by varying the oxygen pressure. Ion scattering studies indicate that the ceria is highly oriented to (111) planes of fluoritic CeO_2. Oxygen deficiency is incorporated as anion vacancies leading to increased Ce cations at the surface. Rh is vapor deposited onto oxidized or reduced ceria films. Synchrotron based soft x-ray photoelectron spectroscopy (SXPS) is used to monitor the ceria oxidation state and to identify surface molecular species. TPD is used to monitor evolved molecular species. We have studied adsorption and co-adsorption of NO, N_2O, CO, O_2, H_2O, SO_2, CO_2, H_2 and C_2H_4. We find that generally ceria is difficult to reduce under UHV conditions. Neither CO nor H_2 will easily reduce the ceria films even in the presence of Rh particles. Even H from dissociated water and ethylene evolves primarily as H_2 rather than reducing ceria. Of the species we have studied only C, derived from decomposition of either CO or ethylene, will reduce ceria. On the other hand, NO, O_2, H_2O and SO_2 are very effective in oxidizing reduced ceria.

SXPS permits the ability to distinguish between different molecular and atomic states present on the surface. For example, adsorption and thermal evolution of NO on reduced ceria results in at least seven different states of nitrogen. These can also be distinguished from NO and atomic N on the Rh particles. This ability, coupled with isotopically labeled NO TPD, has been used to monitor the evolution of N species on the composite surface. We find that the oxidation state of the ceria is of crucial importance in defining the reactivity of the supported Rh particles. Dissociation of NO and CO on the small supported Rh particles are both strongly enhanced by reduction of the ceria. Water principally interacts with the reduced ceria support, but its dissociation and subsequent hydroxyl decomposition are enhanced by the presence of Rh. These are clear examples of metal-support effects. Co-adsorption studies of CO and NO suggest that for a reduced ceria support, CO and atomic N react to form isocyanate. At temperatures above 600 K a carbon and nitrogen complex is formed that stabilizes both C and N from reaction to CO and N_2, their ultimate fate. Co-adsorption of ethylene and NO does not yield isocyanate due to the lack of a stable CO species, but the same carbon-nitrogen complex is the most stable surface state.

Identification of Active Sites and Elementary Steps in the Selective Reduction of NO_x over Fe/MFI and Co/MFI Catalysts

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Higher energy efficiency in automotive transportation is an important national goal; use of lean burn combustion engines is a realistic strategy to achieve it. Introduction at large scale of such vehicles requires that catalysts can be developed that are capable of reducing toxic NO and NO_2, further called NO_x , in gas emissions containing a large excess of oxygen and moisture. For stationary engines, such as power plants, NO_x reduction with methane is desirable. One strategy is chemical reduction of NO_x with hydrocarbons over zeolite based catalysts. Among these, the materials obtained by sublimation of $FeCl_3$ onto the acid form of FMI (also called ZSM-5) hold high promise for automotive engines, while zeolite supported cobalt catalysts are very efficient in NO_x reduction with methane, i.e. for stationary engines. Our research is therefore focused on Fe/MFI and CoMFI catalysts.

A variety of preparations have been compared; the catalysts are tested in a microflow reactor with a feed containing 2000 ppm NO_x, 2000 ppm iso-butane, 3% O_2 and 10% H_2O. Conversions of NO_x to N_2 of 90% have been obtained. A large arsenal of techniques has been used to identify active species in the Fe/MFI and CoMFI catalysts and to unravel the reaction mechanism. The characterization techniques include: FTIR, uv-vis and Mößbauer spectroscopies, EPR, EXAFS, TPR and isotopic labeling.

Isolated ions, mononuclear oxo-ions, multinuclear oxo-ions and oxide particles of Fe or Co have been identified in zeolite cavities. Multinuclear oxo-ions, such as $[HO\text{-}Fe\text{-}O\text{-}Fe\text{-}OH]^{2+}$, appear capable of forming nitrate ions and nitro groups from mixtures of NO and O_2. Such complexes are typical for zeolite supported transition metal ions; their formation explains the specific catalytic propensity of these systems. There are indications that superoxide ions are involved; they have been identified at low temperature with EPR.. The nitrate ions attached to Fe centers in Fe/MFI react with hydrocarbons at low temperature, forming a deposit with active (amine and OR isocyanate) groups. Upon exposing this deposit to NO, formation of N_2 is observed. Isotopic labeling shows that in each N_2 molecule one N atom comes from the deposit the other from the impinging NO.

With N_2O decomposition over these catalysts the phenomenon of isothermal catalytic oscillation is observed. Kinetic analysis of this process over Fe/MFI suggests that the same multinuclear oxo-ion is acting as the active site. Over these sites N_2O disproportionates to NO and N_2. Density functional analysis calculations of other authors working on enzymes with the same binuclear iron complexes suggest that two Fe ions are bridged by a peroxide group.

Model Studies of Automobile Exhaust Catalysis Using Single Crystals of Rhodium and Ceria/Zirconia

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Continued use of internal combustion engines operating on fossil fuels necessitates greatly improved emissions control technologies. The goal of this program is to fill a gap in the fundamental understanding of catalyst activity and durability with respect to the NO_x reduction performance of automotive catalytic converters. We are accomplishing this goal by obtaining detailed chemical kinetics data on idealized but well-characterized catalyst systems useful for understanding the important elementary converter reactions. For example, in recent years we have measured reaction rates and product selectivities over the Rh(100) surface as a function of temperature, CO partial pressure and NO partial pressure, for direct comparison with our previous results on the (111) and (110) surfaces. For the Rh(100) surface we found that the apparent activation energy (E_a) changes with reaction temperature by up to a factor of 2.3 in the range of 528 to 700 K, while E_a remains constant for the Rh(110) and Rh(111) surfaces over the same temperature range. These and other differences are rationalized on the basis of differing steady-state coverages of reaction intermediates that we measure both in-situ (FTIR) and ex-situ (XPS). In particular, we are using the results of recent in-situ FTIR experiments on Rh(100) to probe the role of adsorbed isocyanate that has been observed on both the (111) and (110) surfaces, albeit at dramatically different coverages and reaction conditions. We have also initiated synchrotron vibrational spectrocopic studies of adsorbed NO on Rh on the IR4 beamline at the National Synchrotron Light Source. A critical issue in our mechanistic studies is the location where NO resides during high-pressure reaction on various Rh surfaces. As such, we specifically are interested in the low-frequency region where features associated with Rh-N motions should appear. In addition, we have obtained detailed spectra in the NO stretch region and have new results on the formation of NO dimers on Rh surfaces at high coverages.

A particular focus of our recent studies is on how the catalytic chemistry of Rh is effected by the oxygen uptake, storage, and release processes carried out by the oxygen storage material. For example, we are elucidating and quantifying the mechanisms responsible for the improved performance with the use of ceria-zirconia mixtures relative to ceria alone formulations. For these latter studies, we have prepared and characterized a number of model, single crystal thin films of ceria with and without Zr-doping. In particular, epitaxial films of mixed $Ce_{1-x}Zr_xO_2$ oxides with x • 0.3 have been grown on various single crystal surfaces of $SrTiO_3$ and Y-stabilized cubic ZrO_2 by oxygen-plasma-assisted molecular beam epitaxy. High-energy ion channeling reveals that Zr atoms substitutionally incorporate at cation sites in the CeO_2 lattice for all doping levels, leading to $Ce_{1-x}Zr_xO_2$ solid solutions. Zr 3d and Ce 3d core-level binding energies show that the oxidation state of both Zr and Ce is +4. Angle-resolved mass-spectroscopy of recoiled ions data was obtained for the CeO_2(001) surface. Prior theoretical investigations have suggested that the (1x1) unreconstructed surface, terminated with bulk equivalent layers of either cerium or oxygen, is unstable due to a non-zero surface dipole. In our study, it was experimentally determined that the surface is terminated with 0.5 monolayers of oxygen. This model results in a stable surface with a zero dipole moment. We have been using the model films to explore the effects of Zr doping on the water-gas shift reaction as well as the bulk and surface reducibility. For example, we are investigating the interaction of D_2O with the CeO_2(001) surface. An analysis of TPD and O(1s) XPS data indicates that the surface has a hydroxyl coverage of ~0.9 monolayers for large water exposures at 85 K. This is consistent with a model in which the polar CeO_2(001) surface can also be stabilized by a reduction of the dipole in the top layer via the formation of a full monolayer of hydroxyls. We have also observed dramatic effects of Zr-addition on the ability of ceria to donate oxygen for the low-temperature oxidation of CO on particulate Rh deposited on the model films.

Understanding the Role of Metal/Support Interactions in Automotive Catalysts

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The goal of this research is to develop a fundamental understanding of the relationship between the nanostructure and chemistry of model transition-metal automotive catalysts (so-called three-way catalysts) and their resulting catalytic properties, particularly with regard to NO_X reduction and the role of the metal/support interface. The results of this research are important to the Department of Energy mission in terms of facilitating the development of better automotive catalysts, as well as in establishing a fundamental understanding of the behavior of nanocrystalline metal particles on oxide substrates, a materials combination encountered in many energy-related applications.

In this research, each of the model samples: Pd/alumina, Rh/alumina, Rh/ceria/alumina, Pd/ceria/alumina, and Pd-Rh/alumina was tested as a catalyst for NO+CO, N_2O+CO, and N_2O decomposition reactions. In the NO+CO reaction, the activity of Pd/alumina was similar to that of Rh/alumina, but ceria promoted the Pd catalyst much more than the Rh catalyst. Kinetic results clearly showed the presence of ceria increased the turnover frequency, decreased the dinitrogen selectivity, and altered the NO+CO reaction orders over both Pd and Rh, with the Pd/ceria/alumina catalyst being the most active. In the N_2O+CO reaction, the ceria-promoted Pd catalyst again had the highest activity, but the promotional effect was not as pronounced as for the NO+CO reaction. In all cases, the results indicate that the promotional effects of ceria may be due to a reaction mechanism involving the metal/ceria interface.

In-situ X-ray absorption spectroscopy at the Ce L_{III} and Pd K edges was also used to characterize CeO_x/alumina and Pd/CeO_x/alumina catalysts under reaction conditions. Exposure of supported CeO_2 to 5% CO in He at 673 K reduced about a third of the Ce atoms to the 3^+ formal oxidation state. These atoms were easily re-oxidized by 5% NO in He. The surfaces of the Pd particles were oxidized by NO at 573 K while the core of the particles remained metallic. The surface oxidized Pd particles were completely reduced to the metallic state by CO at 573 K. Results from exposure of the catalysts to a stoichiometric mixture of NO and CO resulted in average Ce and Pd oxidation states between the reducing and oxidizing conditions described above.

Results from high-resolution TEM showed that ceria is not present as a thin layer (monolayer) on the alumina support, but exists as nanocrystalline particles, similar to the transition-metal particles. Thus, the promotional effect of ceria may relate to metal/ceria particle contacts rather than to ceria/alumina or metal/alumina contacts. Analytical TEM results using energy-dispersive X-ray spectroscopy (EDXS) revealed that Ce, Pd and Rh are not uniformly distributed on the alumina support. Analyses of the Pd-Rh alloy on alumina similarly showed the sample to be inhomogeneous, with the alloy particles apparently having undergone phase separation during synthesis. Chemical analysis of individual particles shows that their composition may vary from the surface to center and as a function of particle size. These nanostructural features are being further analyzed to explain the catalytic behavior of the samples.

The PtSn Surface Chemistry Controlling Olefin Formation from Chloroalkanes

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The formation of olefins from chloroalkanes such as 1,2-dichloroethane is an extremely demanding class of reactions. The overall reaction mechanism must include elementary steps such as carbon-chlorine bond cleavage, removal of surface chlorine by hydrogenation and olefin desorption without subsequent hydrogenation. This class of "hydrogen-assisted chlorine elimination" reactions is effectively catalyzed by PtSn surfaces. Naturally, the PtSn atomic ratio and the degree to which the two metals are alloyed on the surface of support influences the overall chemical kinetics. These metal properties have been probed using organometallic synthesis techniques and characterized by Mössbauer spectroscopy and reaction kinetics. This presentation will provide the details of the experimental results in the context of a molecular-level description of both the materials synthesis chemistry and the catalytic chemistry.

Catalysis and Surface Chemistry at BNL: Sulfur Interaction with Metal Surfaces

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The goal of this program is to provide an improved understanding of chemical catalysis by elucidating details of the fundamental properties of molecules, surfaces, and their reactions that are critical to catalysis. In this abstract the fundamental aspects of the sulfur and sulfur containing molecules interactions with model catalysts are discussed. [1]

Synthesis of sulfur films from S_2 gas.[2] Thin stable films of molecular sulfur were prepared by the deposition of S_2 gas from an electrochemical doser on single crystal metal surfaces kept at temperatures below 250 K in vacuum. We have characterized the films by surface sensitive techniques including synchrotron based infrared spectroscopy and have shown that the S_n species present in the sulfur films are converted to cyclooctasulfur molecules (S_8). These sulfur films were shown to be very useful for studying the nature of metal-sulfur interactions, and for preparation of films of metal sulfides.

Atomic View of Sulfur Interactions with Bimetallic Surfaces: For Cu, Ag and Au metals deposited on ruthenium surface, a small surface concentration of sulfur has a dramatic effect on their nucleation and growth. Layer by layer growth has changed to growth of three-dimensional islands with the mean island densities increased by several orders of magnitude. Sulfur adsorption on the first layer of gold leads to a dispersion of large two-dimensional Au islands into very small 3D clusters immobilized within the outline of the original island.[3]

We identified and measured the forces responsible for self-organization of a nearly perfect triangular lattice of nanometer-sized vacancy islands created by sulfur interaction with a single monolayer of silver on the ruthenium (0001) surface. By using time-resolved STM to monitor thermal fluctuations of the center of mass of the vacancy islands around their final position, we obtained the elastic constants of the lattice and showed that the weak forces responsible for its stability can be quantified.[4]

The early stage of interaction of sulfur with a two-monolayer thick copper film started at the striped phase dislocation edges where sulfur atoms chemisorbed in the pseudo four fold hollow sites. Additional sulfur attacked the stripes, forming a close-packed array of the Cu dislocation loops and the S equilateral triangles. Sulfur generated new threading dislocations, a process forbidden in bulk, thus relieving strain in the thin films. This significant restructuring of the surface preceded the onset of chemical reaction that commenced only at S coverages above 0.25 monolayer. These experiments showed that strain has a significant effect on adsorption and surface reactivity.[5]

Reaction of SO_2 with mono- and bimetallic surfaces.[6-8] In order to minimize the negative effects of sulfur dioxide in environmental pollution, corrosion and catalysis, one has to understand at a fundamental level the interaction of sulfur with metal and oxide surfaces. The chemistry of sulfur dioxide on Pt(111), Rh(111), Ru(001) and Mo(110) was examined. On all these surfaces, the molecule dissociates or transforms into SO_3 or SO_4 species. The reactivity of the metals increases in the sequence Mo < Ru < Rh < Pt. Bimetallic bonding can reduce the sensitivity of a metal for sulfur poisoning by SO_2 as shown in the Sn/Pt and Pd/Rh systems.

Future Research. Time-resolved variable-temperature STM opens new opportunities for fundamental studies of surface interactions and phenomena underlying catalytic activity. Metal on metal growth, surface alloying, metal on metal oxide growth, morphology and stability of bimetallics, reactivity of these models and two-dimensional surface reactions on well-defined surfaces are just a few areas where imaging will have a great impact. The use of the synchrotron-based techniques on same model catalysts can provide an unprecedented synergy in the field of surface science and greatly enhance our understanding of chemical transformation on atomic and molecular level.

Select Publications

1. J.A. Rodriguez and J. Hrbek, Acc. Chem. Res., **32**, 719-728(1999). "Interaction of Sulfur with Well-Defined Metal and Oxide Surfaces: Unraveling the Mysteries behind Catalyst Poisoning."
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Catalysis and Surface Chemistry at BNL: Desulfurization Processes on Oxide and Sulfide Surfaces

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The main objective of this program is to obtain a fundamental understanding of the chemistry of sulfur-containing molecules on oxides and sulfides employed in desulfurization processes carried out in the oil and chemical industries. This can help to minimize the energy losses associated with the poisoning of industrial catalysts by sulfur and prevent the negative effects of SO_x species in the atmosphere. The program makes extensive use of synchrotron-based techniques (photoemission, x-ray absorption spectroscopy, time-resolved x-ray diffraction) and computer modeling (DFT or ab initio Hartree-Fock quantum-chemical calculations).

In the last three years, we have studied several topics related to HDS and DeSOx reactions on sulfides and oxides: basic interactions associated with the bonding of sulfur adatoms, activity of model NiMoS HDS catalysts, correlation between electronic properties and performance of oxide sorbents, cesium as a promoter in desulfurization, chemistry of SO_2 on oxide surfaces, role of Cu in DeSOx operations, etc.

In oil refineries NiMoS catalysts are frequently used for the hydrodesulfurization of organosulfur impurities present in petroleum-derived feedstocks. The properties of these catalysts are not well understood. Our results for the adsorption of thiophene on model MoS_x and Ni/MoS_x catalysts indicate that Ni promotes the bonding on thiophene on the surface, but the presence of H is necessary to induce breaking of the C-S bonds (desulfurization).

In order to obtain a better understanding of the interaction of sulfur-containing molecules with oxide surfaces, the adsorption of H_2S and S_2 was studied on a series of oxides: Al_2O_3, MgO, Cr_2O_3, Cr_3O_4, ZnO, and Cu_2O. The sulfur-containing molecules interact mainly with the metal centers of these systems. The strength of the adsorbate-surface interactions depends on the size of the band gap of the oxide substrate. A simple model based on perturbation theory and band-orbital mixing is able to explain the differences in the reactivity of the oxides. Thus, the chemical activity of an oxide depends mainly on how well its bands mix with the orbitals of H_2S or S_2. The electrostatic interactions between the Madelung field of the oxide and the dipole moment of the admolecule play only a secondary role in bonding.

Recently, we have found that promotion with Cs or Cu largely increases the reactivity of oxides towards sulfur dioxide and other sulfur-containing molecules. The Cs and Cu adatoms facilitate the cleavage of C-S or S-O bonds by providing electronic states that are very efficient for interactions with the LUMO of the adsorbed molecules.

In the near future we plan to perform similar studies on mixed-metal oxides and metal carbides. Mixed-metal oxides play a relevant role in many areas of chemistry, physics and materials science. Several variables can be adjusted to control the performance of a mixed-metal oxide.Recent work indicates that metal carbides have the potential for replacing sulfides in hydrodesulfurization processes with a substantial increase in catalytic activity.

Selected Publications

1. "Interaction of Hydrogen and Thiophene with Ni/MoS_2 and Zn/MoS_2 Surfaces: A Molecular Orbital Study", J.A. Rodriguez, J. Phys. Chem. B, 101 (1997) 7524-7534.

2. "Characterization of Pure and Sulfided $NiMoO_4$ Catalysts using Synchrotron-based X-ray Absoption Spectroscopy (XAS) and Temperature Programmed Reduction (TPR)", S. Chaturvedi, J.A. Rodriguez and J.L. Brito, Catal. Lett. 51 (1998) 85-98.

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4. "Chemistry of Thiophene on ZnO, S/ZnO and Cs/ZnO Surfaces: Effects of Cesium on Desulfurization Processes" T. Jirsak, J. Dvorak and J.A. Rodriguez, J. Phys. Chem. B, 103 (1999) 5550.

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Novel Catalysts for Advanced Hydroprocessing: Transition Metal Phosphides

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The petroleum refining industry is currently faced with a dual challenge: stringent regulations that require a reduction of sulfur levels in transportation fuels, and a decline in the quality and availability of feedstocks. It has been recognized that current hydrotreating catalysts are not able to meet these requirements, and this has given rise to a widespread research effort to try to develop a new generation of catalysts.

This project deals with the study of a novel class of hydroprocessing catalysts that differ fundamentally from existing sulfide-based catalysts. The new materials are the phosphides of transition metals, a class of robust metallic substances that include VP, NbP, MoP, WP, ReP, FeP, CoP, and Ni_2P. These materials have ideal properties for catalysis; they are physically strong and chemically stable, and inexpensive to prepare and regenerate. Initial tests in a trickle bed reactor at realistic conditions show that certain compositions are substantially more active than a commercial sulfided $Ni\text{-}Mo\text{-}S/Al_2O_3$ in the hydrodesulfurization (HDS) of dibenzothiophene and the hydrodenitrogenation (HDN) of quinoline. Moreover, the phosphides are tolerant of sulfur and stable for over 100 h.

A goal of the research is to gain insight on the mechanism of HDN, the most difficult of the hydroprocessing reactions. The role of acid/base reactions is assessed by *in situ* reaction probes. These consist of a series of amines with different structures (different numbers of α and β hydrogens) that are expected to react differently depending on properties of the surface. This allows determination of whether HDN occurs by elimination or displacement. The results are related to the acid and base sites observed on the surface by the infrared spectroscopy of probe molecules and quantitated by adsorption and temperature-programmed reaction techniques. Overall, the suggested research does not involve incremental improvement of a known technology, but exploration of a completely new alternative.

Millisecond Chemical Reactors

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Extremely short contact time chemical reactors offer exciting prospects for the conversion of light alkanes into fuels and chemicals by catalytic partial oxidation. These processes have great promise for the utilization of abundant light alkanes in remote locations. These reactors operate autothermally and adiabatically so that reaction times are extremely short and no external process heat is required. We have shown that these reactors are very efficient in the production of synthesis gas from methane and for partial oxidation of ethane to ethylene. These reactors can be made to produce highly nonequilibrium products because the reaction is initiated and quenched in very short times to that the primary products survive and do not undergo subsequent reactions or homogeneous chain reactions which produce combustion products and carbon.

We will describe four recent specific projects: (1) maximizing yields of syngas from methane and higher hydrocarbons, (2) high yields of ethane from ethylene, (3) production of oxygenates directly from alkanes in a single gauze reactor, and (4) use of laser induced fluorescence to measure free radical intermediates in catalytic oxidation processes at atmospheric pressure.

We will also describe recent experiments in which millisecond catalytic reactors are used for combustion without flames which would produce high levels of pollution. We can also use millisecond reactors for very efficient heat exchange to run-exothermic-endothermic reactions in compact reactor configurations.

Finally, we will also describe detailed modeling of these processes using full two-dimensional descriptions of fluid flow and heat and mass transfer in these systems with complete surface and homogeneous reaction rates to simulate the detailed behavior of the experiments.

Activation of Methane by Size-Selected Iron Cluster Cations: Fe_n^+ ($n = 2 - 15$)

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The thermochemistry of organic fragments bound to metal surfaces is important in understanding a variety of catalytic transformations of industrial importance. However, experimental data on such species is sorely lacking. We address this by studying the kinetic energy dependences of the reactions of Fe_n^+ ($n = 2 - 15$) with CD_4 in a guided ion beam tandem mass spectrometer in the energy range of 0 - 10 eV. All reactions observed are endothermic and form two main products, Fe_nD^+ and $Fe_nCD_2^+$. These primary products decompose at higher energies to form the secondary and higher order products, Fe_nCD^+, Fe_nC^+, $Fe_{n-1}D^+$, $Fe_{n-1}CD^+$, and $Fe_{n-1}C^+$. The cross section magnitudes for the dehydrogenation product, $Fe_nCD_2^+$, are observed to vary considerably as a function of cluster size. Thresholds for the various primary and secondary reactions are analyzed and bond energies for iron cluster cation bonds to C, CD, and CD_2 are determined. Their relative magnitudes are consistent with simple bond order considerations. As a function of cluster size, these bond energies rapidly reach relatively constant values, which are probably close to the bulk phase values. On the basis of this thermochemistry, we find that the there is a barrier to the dehydrogenation reaction for the iron dimer cation, similar to that found for reaction of atomic Fe^+ with methane. For all larger clusters, there is no barrier to the dehydrogenation reaction and double dehydrogenation becomes the dominant low energy process.

Oxidative Dehydrogenation of Alkanes on Supported Oxide Domains: Structural Requirements and Reaction Pathways

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Support (Al_2O_3, SiO_2, HfO_2, TiO_2, and ZrO_2) and alkali effects on the structure of supported MoO_x, VO_x, WO_x and on their behavior in alkane oxidative dehydrogenation (ODH) were examined over a wide range of oxide surface density (0.5-30.0 MO_x/nm^2). X-ray absorption, Raman, and UV-visible spectra showed that MO_x structures evolved from isolated monomers to oligomers and ultimately to oxide clusters as surface density increased. On VO_x domains, ODH turnover rates (per V) reached a maximum on domains of intermediate size, which provide a compromise between VO_x reducibility and accessibility. Turnover rates on polyvanadates and bulk V_2O_5 surfaces were very similar. Interactions of VO_x species with supports determine the VO_x structure prevalent for a given surface density, but do not appear to influence ODH rates on exposed VO_x sites. Rate constants for propane dehydrogenation and for secondary propene combustion were influenced similarly by VO_x structure, suggesting that these reactions require similar VO_x sites, which exist in VO_x domains of any size.

MoO_x supported on ZrO_2 also evolved from isolated monomolybdates to polymolybdates and ultimately to MoO_3 and $ZrMo_2O_8$ as surface density and treatment temperature increase. Below 5 MoO_x/nm^2, only polymolybdates were detected after treatment below 873 K. Above 5 MoO_x/nm^2, low temperatures (<723 K) give MoO_3 and higher temperatures lead to reactions between MoO_3 and ZrO_2 to form $ZrMo_2O_8$. Oxidative dehydrogenation rates (per Mo) decreased with increasing surface density because of the combined effect of stronger Mo=O bonds and lower MoO_x dispersion. Strong M=O bonds lead to slower rates of C-H activation, of ODH, and of reduction in H_2. This correlation between reducibility and ODH rates is consistent with the effects of alkali on ODH rates and selectivity.

Kinetic and isotopic studies were used to probe elementary steps in C_3H_8 ODH on VO_x and MoO_x. Rate expressions on both catalysts were similar and consistent with rate-determining C-H activation steps using lattice oxygen. Isotopic studies led to similar conclusions on VO_x and MoO_x; only the results on VO_x are shown here. Reactions of C_3H_6-$CH_3{}^{13}CH_2CH_3$ confirmed the sequential-parallel ODH-combustion pathways proposed from residence time studies. Reactions of ${}^{18}O_2/C_3H_8$ on $V_2{}^{16}O_5$ led to ${}^{16}O$ from the lattice in CO and CO_2. ${}^{16}O{}^{18}O$ did not form during C_3H_8-${}^{18}O_2$-${}^{16}O_2$ reactions because O_2 dissociation is irreversible. C_3H_8-C_3D_8-O_2 mixtures led to products without $C_3H_{8-x}D_x$ formation, because C-H activation steps are also irreversible. Quasi-equilibrated OH recombination steps led to rapid cross-exchange in C_3H_6-D_2O. Normal ODH kinetic isotopic (KIE) effects ($k_H/k_D=2.5$) were slightly larger than for C_3H_8 or C_3H_6 combustion (1.7, 2.2), consistent with C-H kinetically-relevant steps. KIE measurements using $CH_3CH_2CH_3$ and $CH_3CD_2CH_3$ showed that methylene C-H bonds in propane and allylic C-H bonds in propene are involved in the initial C-H activation steps for both ODH and combustion reactions. A redox mechanism involving two lattice oxygen atoms in the activation of C-H bonds accurately describes the kinetic effects of H_2O, C_3H_8, and O_2 and the isotopic results on both MoO_3 and V_2O_5 catalysts.

A Study of Catalysts and Mechanisms in Synthesis Reactions

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Research Scope and Objectives

The importance of surface-generated gas-phase radicals in catalysis has been the focus of the research under this project. Recent emphasis has been on the reactions of hydroxyl radicals with surfaces which are factors in such diverse phenomena as catalytic combustion, aqueous photocatalysis, atmospheric chemistry and the preparation of microelectronic devices.

Reactions of Hydroxyl Radicals on Titania, Silica, Alumina, and Gold Surfaces

Previous work has shown that during the oxidative coupling of methane, methyl radicals which are formed on a catalytic surface enter the gas phase where they may couple to form ethane, or they may react back with the surface and subsequently be converted to carbon dioxide. Thus, secondary reactions of the radicals with the surface are important in the overall selectivity. Many of the same catalysts that are capable of forming methyl radicals also produce hydroxyl radicals from the reaction of H_2O with O_2 at elevated temperatures. In order to determine the importance of the radicals in such processes as catalytic combustion, it is necessary to know the extent to which these radicals react on or with a surface. The reactions of hydroxyl radicals with titania, silica, alumina and gold surface have been studied and the reaction probabilities at *ca.* 300 K have been measured.

The OH^- radicals were produced from H_2O in a microwave cavity and were allowed to react on the surfaces in a tubular flow reactor. The concentration of radicals, as determined by laser-induced fluorescence (LIF) spectroscopy, is such that monolayer coverage would be achieved in several seconds; therefore, the measured steady state disappearance of the radicals is attributed to a surface recombination of the radicals to form H_2O_2. The production and decomposition of H_2O_2 becomes an important aspect of the OH^- reaction probability, and in a separate experiment, the decomposition of aqueous H_2O_2 was examined over the same surfaces.

At 308 K, the OH^- reaction probabilities were 2×10^{-4} for TiO_2 (anatase and rutile), 2×10^{-3} for SiO_2, 5×10^{-3} for α-Al_2O_3 and $>3 \times 10^{-2}$ for Au. The relative rate of H_2O_2(aq) decomposition was found to follow the sequence Au > α -Al_2O_3 > $TiO_2 \approx SiO_2$, which, except for TiO_2, follows the sequence found for the OH^- radical reaction probability. For all of the materials except TiO_2, a radical mechanism is proposed which describes a common set of reactions for the removal of $OH^-$and the decomposition of H_2O_2. The first step in this mechanism is the coupling of OH^- radicals to form H_2O_2. The overall rate of reaction for both OH^- removal and H_2O_2 decomposition depends on the concentration of OH on the surface. A theoretical analysis using a cluster model for an Au surface has shown that the OH-Au chemisorption bond is dominantly ionic, with the OH radical becoming an OH^- anion. The adsorption energy may be as large as 155 kJ mol^{-1}. With TiO_2 as a catalyst and H_2O_2 as a reagent, an alternative mechanism that involves redox chemistry is believed to occur. Over this oxide, the OH^- radical reaction probability of only 10^{-4} probably results from a small adsorption energy or sticking probability. In photocatalytic applications for the destruction of organic materials, OH^- radicals that are formed on TiO_2 would remain available as reactive intermediates.

Future Research

Although the effect of temperature on the reaction probabilities is small under the conditions of these studies, there is a need for experiments to be carried out at much higher temperature (*e.g.*, 1200 K) so that the importance of the hydroxyl radicals in catalytic combustion can be determined.

Mediation of Heterogeneous Oxidation of Aliphatic Hydrocarbons Through System Specific Optimization of Photo-Induced Charge Carrier Separation Distance on Tio$_2$, Pt/Tio$_2$ and Iron Oxide/Tio$_2$ Particulate Photocatalysts

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Our research has as its primary practical objective the energy efficient heterogeneous oxidative photo-degradation of organic pollutants, and synthesis of commodity chemical from aliphatic hydrocarbons. Pollution remediation with wide band semiconducting particulate and nano-porous photocatalysts is at the present time a demonstrably viable process [1, 2] capable of helping to address challenges such as the cleanup of DOE, military and Superfund sites around the country, whose estimated cost was reported to be about $650 billion [3], despite concerted efforts by many academic, commercial and government organizations over the past five years. In addition to the photo-degradation of organic substrates, we also anticipate using mechanistic information gleaned from the present investigation as the basis for synthetic studies, such as the goal of using O_2 in the heterogeneous photo-oxidation of aliphatic or cyclic hydrocarbons to higher value oxo chemicals. Recombination of photoelectrons with photoholes is traditionally considered a major cause for low quantum efficiencies in heterogeneous photocatalytic processes. Based largely on intuitive reasoning, it has frequently been assumed in the literature that maximized efficiency can be achieved by increasing the charge carrier separation distance (CCSD), thereby decreasing the probability of recombination prior to reaction of the desired chemical reagents with photoelectrons and photoholes. To test this assumption, we have employed the time resolved photocharge technique (TRPC) to measure CCSD of nano-dimensioned heterogeneous photocatalysts, such as Pt/TiO$_2$ with various amounts of photolytically deposited Pt, and found that CCSD increases with increasing % Pt, goes through a maximum and then decreases. Introduction of gaseous CH_3OH + O_2 to these Pt/TiO$_2$ catalysts and exposure to UV light results in optimum CH_3OH oxidation efficiency and production of methylformate. Catalysts with % Pt content yielding a maximum CCSD are observed to closely coincide with the corresponding photocatalytic maxima [2, 4]. As a means of testing the generality of the conclusion that optimized rather than maximized CCSD is a dominant factor in improving photo-oxidation efficiency in these heterogeneous systems, we have made a major redesign of the TRPC apparatus, which provides for controlled environments during measurement, i.e., vacuum; controlled atmosphere (inert or reactive); temperature control (-100 to + 150 C), and lowered background noise by inclusion of light traps fabricated from non-photoconducting materials. This apparatus makes possible, for the first time, the measurement of the intrinsic charge carrier dynamics of photoconducting materials in vacuum and allows for in-situ determinations during photocatalysis in reactive atmospheres. The catalysts under investigation are initially composed of Pt/TiO$_2$ and iron oxide/TiO$_2$, with various amounts of controlled distributions and morphologies of Pt and iron. For each system we strive to achieve a broad range of CCSD on both sides of maximum values. The organic substrates consist of C6 and C8 aliphatic and cyclic compounds. These investigations will allow a critical appraisal of earlier mechanistic conclusions, which place considerable importance on the proximal occurrence on the catalyst surface of the initial reaction products of photoelectrons with O_2 and photoholes with the organic substrate, thereby lending support for a Russell-like mechanism for the formation of oxygenated products [2,3]. This radical mechanism is also confirmed in homogeneous Gif-type oxygenation of hydrocarbons [5].

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Methanol: A “Smart” Chemical Probe Molecule

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It is important to develop a “smart” chemical probe molecule that will further enhance the information obtained via high-throughput catalyst screening methodologies. Such a “smart” chemical probe molecule for heterogeneous metal oxide catalysts is CH_3OH since it can provide quantitative fundamental information about the number of surface active sites as well as the distribution of different surface sites (e.g., redox, acidic and basic). A novel chemisorption method will be presented that employs the dissociative adsorption of methanol to surface methoxy intermediates in order to *quantitatively determine the number of surface active sites* on metal oxide catalysts. Furthermore, the methanol oxidation product distribution at low conversions reflects the *nature of the surface active sites* on metal oxides since redox sites yield H_2CO, acidic sites yield CH_3OCH_3 and basic sites yield CO_2. In addition, the commonality of the surface methoxy intermediate during dissociative chemisorption of methanol and methanol oxidation on oxide catalysts also allows for the *quantitative determination of the turnover frequency* (TOF) values.

Methanol dissociative chemisorption and oxidation were employed to characterize a wide range of one component metal oxide catalysts (CoO, Cr_2O_3, MnO, CuO, NiO, V_2O_5, ZnO, SnO_2, Fe_2O_3, HfO_2, MoO_3, WO_3, CeO_2, ZrO_2, Sb_2O_3, Al_2O_3, Nb_2O_5, Ta_2O_5, TiO_2 and SiO_2). The number of surface active sites for methanol dissociative adsorption mostly corresponded to ~3 umol/m^2 for the metal oxide catalysts. The distribution of different types of surface sites was found to vary widely with the specific metal oxide catalyst. The TOF values for the metal oxide catalysts were found to vary over six orders of magnitude (10^{-2} to 10^{+4} sec^{-1}). An inverse relationship was found between the methanol oxidation TOF values and the decomposition temperature of the surface $M\text{-}OCH_3$ species because the decomposition of the surface $M\text{-}OCH_3$ species is the rate-determining-step during these reactions.

The above methodology was further extended to molybdate mixed metal oxide catalysts ($TiMoO_5$, $MnMoO_4$, $Cr_2(MoO_4)_3$, $Al_2(MoO_4)_3$, $Zr(MoO_4)_3$, $Fe_2(MoO_4)_3$, $NiMoO_4$, $CoMoO_4$ and $CuMoO_4$). The number of surface active sites for methanol dissociative adsorption also corresponded to ~3 umol/m^2. Methanol oxidation over the molybdate catalysts primarily yielded redox products and the TOF (redox) values were very similar to that for pure MoO_3. These observations suggest that molybdate mixed metal oxide catalysts are enriched in surface Mo and may actually possess a surface molybdenum oxide overlayer. The metal oxide cations were found to affect the surface Mo sites via a ligand effect. These new insights account for the special properties of bulk metal molybdates during catalytic oxidation reactions as well as their molecular design.

Combinatorial Materials Science: Accelerating Materials Discovery and Optimization Processes

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In many respects materials science and related fields are driven by the discovery process. Combinatorial chemistry, the technique of creating vast numbers of compounds by reacting a set of components in all possible combinations at once, holds tremendous promise for greatly accelerating materials discovery and optimization processes. This approach, adopted nearly universally by the pharmaceutical industry in their search for new drugs, does, however, require a significantly altered strategy when applied to the materials sciences that impact the chemical and electronics industries. For example, synthetic strategies in these industries, unlike pharmaceuticals, vary from thin film methods such as physical and chemical vapor deposition, to more traditional bulk techniques, to the use of electrochemical methods. Screening strategies can also vary widely, depending upon the targeted application of the material. Thus, a major challenge in combinatorial materials science is the development of not only a diverse set of synthetic strategies but also screening strategies that can quickly assess the chemical, optical, mechanical, and electronic properties of large arrays of materials. Clearly, it is far from a simple matter to overlay the techniques and strategies developed for pharmaceutical research and drug discovery to those appropriate for catalysts, polymers, and electronic materials; indeed it is impossible. Rather, one must start afresh in developing entirely new technologies. Work over the past few years strongly suggests that combinatorial approaches to materials discovery will ultimately be successful, leading to significant technological breakthroughs impacting a variety of industries. In this presentation recent developments in combinatorial materials science will be reviewed, and opportunities and challenges for continued progress in this rapidly expanding field will be discussed.

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Automotive Exhaust Catalysis

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The development of catalysts for the treatment of automotive exhaust has, over the years, proceeded in a relatively continuous fashion, driven largely by the need to steadily attain ever lower levels of regulated emissions. Presently, however, the additional need to improve fuel economy and decelerate the production of carbon dioxide is stimulating intense effort to create entirely new technologies that are effective for lean combustion. This talk will describe recent work at Ford on both stoichiometric and lean-combustion catalysis, including control of cold-start emissions, catalysts for diesel exhaust, nitric oxide traps, plasma-assisted catalysis, and computational efforts to model fundamental reaction mechanisms.

The Roadmap for Catalysis Science in the 21st Century

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The future focus of catalysis research is to achieve 100 percent selectivity in chemical processes. Environmental concerns for clean air, water, and soil, reasons of thermodynamic efficiency, the need for developing chiral chemistry, and demands for lowering costs of manufacturing all fuel this trend. To achieve it, better understanding of selectivity on the molecular scale is needed along with the fabrication of high technology catalysts with complete control of the variables that determine selectivity.

Catalysis that occurs under extreme conditions should be explored. This includes high temperature (>1000° C), short contact time (~10 msec) reactions, and catalytic reactions that occur on the ocean floor. The catalytic conversion of methane should be a national commitment as it is the likely feedstock for fossilized chemicals for the next century. Studies of correlations between heterogeneous, homogeneous, and enzyme catalysis are likely to merge these fields and could lead to new directions of catalysis science. Technique developments will focus on achieving better time resolution and spatial resolution so that surface reaction dynamics can be monitored on ever shorter time scales and on the nanoscale.