

SOUTHWEST CATALYSIS SOCIETY

2013 SPRING SYMPOSIUM

Friday, April 26, 2013

Grand Hall of the Ley Student Center
Rice University, Houston, TX



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The SWCS officers and I welcome you to the 2013 SWCS Spring Symposium, **Friday, April 26, 2013**, at Rice University in the Grand Hall of the Ley Student Center (building #43 on the Rice University map on the back page).

We are delighted to present 6 invited speakers and 27 poster presentations for this year's meeting. Meritorious posters presented by students and post-docs will be identified with **Best Poster Awards**, carrying cash prizes.

The 2013 Spring Symposium **registration fee is \$50**, which includes North American Catalysis Society and SWCS yearly membership dues, along with coffee/snack breaks. To speed registration, provide your business card along with your registration fee.

We will be able to accept credit cards (Visa, MasterCard, Discover, and American Express) for the registration fee or corporate donations. Credit card receipts will be sent via e-mail, so please be prepared to input your e-mail address into our system when you pay. But note, that checks are faster (especially if you have them ready to go). We will also continue to accept cash.

Do let those who cannot attend the Symposium know to mail in their membership due (\$40) to our Treasurer, John Novak (mailing address shown at left).

Checks should be made out to SWCS.

The student registration fee is \$10, which includes NACS and SWCS membership.

PARKING: The best place to park is in the central campus garage marked on the map (last page) across from the student center. You will need a credit card to enter. We will have parking coupons available for drivers of cars to exit the garage for free. You will input the coupon upon exiting, then run your credit card, which will not be charged.

Enjoy!

Andy Moreland
Valero Energy Corporation
Chair

2013 PROGRAM

All talks & breaks will be held in the Grand Hall of the Ley Student Center

- 7:30 AM** **Registration – John Novak, Treasurer (& helpers)**
- 8:25 AM** **Welcoming Remarks – Andy Moreland, Chair**
- 8:30 AM** **Doron Levin, ExxonMobil, Annandale, NJ**
"Advances in Hydroprocessing Catalyst Technology: The Discovery of ExxonMobil/Albemarle's Nebula Catalyst"
- 9:00 AM** **Dedication of Symposium to Prof. Wayne Goodman**
- 9:15 AM** **Jerry Spivey, LSU Cain Department of Chemical Engineering, Baton Rouge, LA**
"Natural Gas to Syngas Using Rh-Substituted Pyrochlore ($\text{La}_2\text{Zr}_2\text{O}_7$) Catalysts"
- 9:45 AM** **Coffee Break**
- 10:05 AM** **Tushar V. Choudhary, Phillips 66, Bartlesville, OK**
"Developing HDS Understanding Based on Real Feed-Stocks"
- 10:35 AM** **Li Liu, Department of Chemistry, Texas A&M University**
"Nanostructured Gold Model Catalysts on Oxygen-free Substrates"
- 11:05 AM** **Southwest Catalysis Society Excellence in Applied Catalysis Award**
James "Jerry" Spivey, LSU Cain Department of Chemical Engineering
- 11:20 AM** **Lunch Break (on your own) Rice Student Center**
- 12:45 PM** **Kim Johnson, Shell Chemical Co., Houston, TX**
"Shell Alternative Transport Fuels"
- 1:15 PM** **Lars C. Grabow, University of Houston, TX**
"From Hydrodesulfurization to Hydrodeoxygenation: What are the similarities at the atomic-scale?"
- 1:45 PM** **Coffee Break – Poster Session setup**
- 2:00 PM** **Poster Session**
- 3:15 PM** **Poster Awards and SWCS Business Meeting**
Grand Hall – Ley Student Union
- 3:30 PM** **Adjourn**

Advances in Hydroprocessing Catalyst Technology: The Discovery of ExxonMobil/Albemarle's Nebula Catalyst

Doron Levin

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The discovery and development of the Nebula catalyst, the world's most active hydrotreating catalyst, was an unusual journey that began with an unexpected result during the research of a summer intern at Exxon's Corporate Research Labs. Research into the pillaring of layered double hydroxides related to hydrotalcite resulted in the discovery of an unusual chimie douce reaction that produced novel mixed oxide phases. It was then discovered that isostructural nickel molybdate phases could be produced by direct precipitation routes which opened the door for the development of the Nebula catalyst. This presentation will highlight the discovery phase of the catalyst, and demonstrate how this work led to the commercialization of the Nebula catalyst which is used in refineries around the world today.

Natural Gas to Syngas Using Rh-Substituted Pyrochlore ($\text{La}_2\text{Zr}_2\text{O}_7$) Catalysts

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The conversion of methane to syngas via CO_2 reforming requires temperatures above 900°C and is inevitably accompanied by carbon deposition. Pyrochlores are thermally stable crystalline metal oxides into which catalytically active metals such as Rh can be isomorphically substituted. Methane TPD and kinetic results suggest a mechanism in which methane dissociates on Rh sites, and CO_2 reacts with surface H_2O that is formed from hydrogen spillover and reaction with surface oxygen.

Developing HDS Understanding Based on Real Feed-Stocks

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From the viewpoint of efficient production of clean fuels it is important to optimize key processes such as sulfur (HDS) removal from different petroleum fractions. Improvements typically require a good understanding of the reaction chemistry. Unfortunately due to the complex nature of

petroleum feed-stocks developing a realistic understanding of the reaction chemistry is quite challenging. Herein our effort towards understanding HDS chemistry of heavy gas oils is reviewed. The work is also discussed in context to the HDS chemistry of diesel boiling range feeds. The practical relevance of these studies including validation using commercial data will also be discussed briefly

Nanostructured Gold Model Catalysts on Oxygen-Free Substrates

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This talk is dedicated to the memory of Wayne Goodman.

Nanostructured gold model catalysts have been synthesized on a variety of graphene and boron nitride (BN) thin film substrates supported on refractory metals. STM studies showed that Au forms two-dimensional (2-D) islands on graphene/Ru(0001) and small clusters on BN/Rh(111). The electronic structures of these gold nanostructures have been characterized by electron energy loss spectroscopy (EELS) and angle resolved photoemission spectroscopy (ARPES), and their geometric structures have been studied by scanning tunneling microscopy (STM) and density function theory (DFT) simulations. CO and O₂ were used to probe the activity of these gold model catalysts. On 2-D gold islands, adsorbed CO molecules demonstrate a characteristic stretching frequency and can be titrated by O₂ molecules. On BN/Rh(111) substrates, active O₂ adsorption occurs only on small gold clusters deposited at liquid N₂ temperature, demonstrating a particle-size dependent reactivity.

Southwest Catalysis Society Excellence in Applied Catalysis Award

James “Jerry” Spivey, LSU Cain Department of Chemical Engineering

Shell Alternative Transport Fuels

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World demand for energy is growing fast. The combination of population growth and economic development could result in a doubling of energy demand by 2050. Transportation fuels accounts for a quarter of global energy use and energy-related CO₂ emissions. All fuel and drive train options will be needed. Biofuels can offer a low ‘well-to-wheel’ CO₂, sustainable alternative to conventional gasoline and diesel. Biofuels also help diversify the liquid road transport fuel pool and reduce dependence on oil based transport fuels. This offers the prospect of improved energy security – particularly when domestic raw materials are used. Shell is building capacity in biofuels that provide best combinations of performance and low ‘well-to-wheel’ CO₂ performance from more sustainable feedstocks.

From Hydrodesulfurization to Hydrodeoxygenation: What are the Similarities at the Atomic-Scale?

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Fast pyrolysis of biomass is a promising low-cost technology that produces bio-oil suitable for use as transportation fuel after an appropriate upgrade step. The upgrade is necessary to increase the heating value, lower the viscosity and improve the long-term stability, and can be achieved by reducing the oxygen content through hydrotreatment over heterogeneous catalysts. While hydrodeoxygenation (HDO) of bio-oil is an emerging technology, hydrotreating for the removal of sulfur from petroleum products (HDS) has matured over decades and detailed knowledge regarding the catalyst structure, active sites and reaction mechanism are available. Both hydrotreating processes show similarities on the macroscopic scale and the identification of atomic-scale catalytic reactivity descriptors may speed up the discovery of novel HDO catalysts from existing knowledge of HDS chemistry.

Here, we investigate the HDO mechanism of acetaldehyde, a surrogate molecule for the over 400 different oxygenated species in biomass-derived pyrolysis oil, on the Ru(0001) and RuO₂(110) surfaces using Density Functional Theory (DFT) calculations and compare the results to similar studies of thiophene HDS. The surface structure of metal-sulfides and metal-oxides under reaction conditions and the role of surface vacancies as active sites during both, HDS and HDO, are discussed. DFT results indicate that acetaldehyde can be selectively deoxygenated on vacancy sites of RuO₂(110), but metallic Ru favors C-C bond over C-O bond scission, which leads to the unwanted decarboxylation reaction and the formation of carbon deposits.

POSTER ABSTRACTS

1. Enzymatic Hydrolysis of Cellulose by Composite Cellulase/Nafion Fibers

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The hydrolysis of cellulose is a chemical conversion of interest for biofuel production due to the natural high abundance of biomass feedstocks available. Typically this conversion is done chemically or enzymatically. The limiting factor in the use of enzymes for large scale operation is the cost of enzyme. This disadvantage can be minimized by extending the catalytic lifetime of typically short lived enzymes, usually by immobilization. Cellulase enzyme fibers were successfully fabricated through core-shell electrospinning. Composites were also generated using the same technique with a coaxial configuration with cellulase in the inner core and a polymer (Nafion) in the outer shell. Fibers provide a higher surface area when compared to protein immobilized on films, translating to higher active site accessibility and activity. The outer shell Nafion helps to hydrolyze cellulose which then is broken down to glucose by enzymes in the inner core. These fibers can potentially be incorporated as reactive membranes for the production of biofuels using solid substrates under mild conditions.

2. Polymer-Supported Reusable Phosphine Ligands for Palladium Mediated Homogeneous Catalysis

Tatyana V. Khamatnurova, Dongmei Zhang, David E. Bergbreiter
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Reversible addition-fragmentation chain transfer (RAFT) polymerization has been used to prepare alkane-soluble poly(4-alkylstyrene)-bound hindered phosphine ligands. Both *tert*-butyl styrene and 4-dodecylstyrene were copolymerized with 5-10 mol% of 4-chloromethylstyrene using RAFT chemistry to afford poly(*tert*-butylstyrene-*co*-4-dodecylstyrene-*co*-vinylbenzyl chloride) polymers that can undergo substitution of the benzylic chlorine. For example, substitution with dicyclohexylphosphinobiphenyl ligand yields an electron-rich air stable pendant phosphine ligand. Palladium complexes of poly(4-alkylstyrene)-bound phosphines were compared to those formed with a polyisobutylene (PIB), whose terminus was also converted into a dicyclohexylphosphinobiphenyl ligand. Both complexes were active and recyclable catalysts in haloarene-amine and haloarene-arylboronic acid couplings. Additionally, a diphenylstyrylphosphine ligand was incorporated onto the poly(*tert*-butylstyrene-*co*-dodecylstyrene) polymer via RAFT chemistry. The catalytic activity of these polymer-supported phosphine ligands and their recycling will be discussed and compared with similar recovery/reuse of poly(4-alkylstyrene)-bound organocatalysts.

3. Polyolefins as Supports and Solvents in Ru-Catalyzed Metathesis Chemistry

Jakkrit Suriboot[†], Christopher E. Hobbs[†], Yanfei Yang[†], Hassan S. Bazzi[‡], and David E. Bergbreiter[†]
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Recycling of homogeneous catalysts generally and of Ru-catalysts used in metathesis chemistry is an important unsolved problem. This study will discuss how polyolefins and polyethylene (PE_{olig}) in particular can be used as supports and/or solvents to recover Ru-catalysts or separate its residues from products. For example, by using a polyethylene-supported catalyst that is soluble hot and insoluble cold, we have shown that it is possible to effect both ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) reactions with separation of products and catalysts or catalyst residues. In these cases, the quantitative insolubility of these catalysts or its residues and the products' solubility allowed the products to be separated at room temperature as solutions from the insoluble catalysts. These polyethylene-bound second-generation Hoveyda-Grubbs catalysts were formed using *N*-heterocyclic carbene ligands that contained polyethylene oligomers. Based on other work where polyisobutylene-bound (PIB) species that are phase selectively soluble in heptane

have been used for catalyst recovery, other still ongoing work is exploring additional strategies where unfunctionalized polyethylene (Polywax) is used as a solvent in place of heptane to recover either PIB- or PE_{olig}-bound catalysts. Such waxes are low viscosity liquids at ca. 75 °C but separate as solids or gels at room temperature. The results of both of these studies are that products can be prepared with substantially lower Ru contamination. For example, ROMP products have been prepared with 25 ppm Ru residues.

4. Hammett Studies of Benzyl Alcohol Oxidation over Supported Au Catalysts

Luke Tibbitts, Johnny Saavedra, Bert D. Chandler

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This study uses Hammett methodology to explore the electronic effects of metal oxide supports on gold catalysts. The three supported gold catalysts, Au/Al₂O₃, Au/TiO₂, and Au/ZnO, were investigated for the selective oxidation of benzyl alcohol to benzaldehyde at 60 °C. Reactions were held at low conversions in order to obtain initial rates by plotting the aldehyde conversion % versus time. Based on the rates for the substituted benzyl alcohols on each catalyst, a Hammett study was used to determine the support's effect on the reaction. The Hammett plot demonstrated slopes of -0.86 ± 0.05 , -0.44 ± 0.03 , and -0.28 ± 0.02 for alumina, titania, and zinc oxide, respectively. These results show a statistical difference amongst the supports, which illustrates a change in the electronic effect on the catalyst.

5. Thiol Poisoning Studies in Selective Alcohol Oxidation: Evaluating the Number of Active Sites on Traditional and Dendrimer Templated Supported Au Nanoparticle Catalysts.

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Comparing heterogeneous catalysts requires evaluating the number of active sites from one catalyst to the next. Using selective benzyl alcohol oxidation as a model reaction, we developed controlled thiol poisoning methodologies to evaluate the number of active sites in commercial supported Au nanoparticle catalysts. Para-methoxybenzyl alcohol oxidation to the corresponding aldehyde showed a linear decrease in activity when either decanethiol or phenylethyl mercaptan thiol was added to the reaction mixture. For both poisons, catalysis was shut down at about 25 mol% of added thiol (relative to Au). Phenylethyl mercaptan thiol was also used in UV-Visible spectrophotometric titrations of surface Au atoms, providing a rapid laboratory assessment of particle size. The new kinetic and adsorption techniques were compared correlated with TEM data and used to dendrimer removal conditions for PAMAM dendrimer templated Au catalysts.

6. FTIR Studies for Au/TiO₂ Catalyst Used in CO Oxidation: Effect of Activation Conditions in Reactivity and Deactivation

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Activation and reaction conditions (temperature, time, feed composition, etc.) have dramatic effects on the activity of supported gold catalysts. Understanding the influence of thermal activation on catalytic activity is an essential factor in catalyst preparation; however, there is no agreement in the literature regarding activation procedures. The choice of activation conditions is mainly guided by preventing Au nanoparticle sintering. Using a commercially available Au/TiO₂ sample, we found that changing the thermal pretreatment yields a broad range of catalytic activities. This mimics the range of activities reported in the literature (Table 1). To test the effect of thermal activation on catalytic activity, in-situ FTIR experiments were combined with catalytic testing. Potential changes to the Au nanoparticles and to the titania support were monitored; such studies may help shed light onto why different research groups often report Au catalysts with such markedly different activities.

7. A Theoretical and Experimental Examination of Systematic Ligand-Induced Disorder in Au Dendrimer-Encapsulated Nanoparticles

David F. Yancey^{1,2}, Samuel T. Chill^{1,3}, Liang Zhang^{1,3}, Anatoly I. Frenkel⁴, Graeme Henkelman^{1,3}, and Richard M. Crooks^{1,2,*}

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We have developed a new methodology for the analysis of 1-2 nm nanoparticle catalysts using extended X-ray absorption fine structure (EXAFS) spectroscopy. Different numbers of thiols were introduced onto the surfaces of dendrimer-encapsulated Au nanoparticles, consisting of an average of 147 atoms, to systematically tune the nanoparticle disorder. An analogous system was investigated using density functional theory molecular dynamics (DFT-MD) simulations to produce theoretical EXAFS signals that could be directly compared to the experimental results. Validation of the theoretical results by comparing to experiment allows us to infer previously unknown details of structure and dynamics of the nanoparticles. Additionally, the structural information that is learned from theoretical studies can be compared with traditional EXAFS fitting results to identify and rationalize any errors in the experimental fit. This study demonstrates that DFT-MD simulations accurately depict complex experimental systems in which we have control over nanoparticle disorder, and shows the advantages of using a combined experimental/theoretical approach over standard EXAFS fitting methodologies for determining the structural parameters of metallic nanoparticles. This approach is applicable to a wide variety of cases in which nanoparticle catalysts are monitored *in-situ* with X-ray absorption spectroscopy.

8. An Experimental and Theoretical Investigation of the Inversion of Pd@Pt Core@Shell Dendrimer-Encapsulated Nanoparticles

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The homogeneous synthesis of core@shell Pd₁₄₇@Pt₁₆₂ dendrimer-encapsulated nanoparticles (DENs) and the subsequent inversion of the nanoparticles to form a Pt₁₄₇@Pd₁₄₇Pt₁₅ structure is reported here. The key finding is that the final inverted structure, determined by *in situ* extended X-ray absorption fine structure (EXAFS) spectroscopy, correlates well with first-principles theoretical calculations. DFT calculations predict that the inverted Pt₁₄₇@Pd₁₄₇Pt₁₅ structure is more thermodynamically stable than the original Pd₁₄₇@Pt₁₆₂ structure. This inversion is not observed in literature reports of larger core@shell nanoparticle structures, and is also seen in this work of 1.7 nm Pd₅₅@Pt₉₂, implying this is a size related phenomenon. We also present theoretical evidence that the increased disorder and high energy edge and corner sites that are present in these DENs of 2.0 nm and smaller help initiate rearrangement to the more stable structures (Pt₁₄₇@Pd₁₄₇Pt₁₅ and Pt₅₅@Pd₅₅Pt₃₇).

9. Catalysts for the Double-Bond Isomerization of Long Chain Olefins

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This project examines the double-bond (positional) isomerization of long-chain (C16-C18) olefins. The goal is to make highly internal olefins from 1-olefin feeds. Internal, long chain olefins are used in the manufacture of paper sizing agents and as deep-sea drilling fluids. Both solid acid and organometallic chain-walking catalysts are being examined. Solid acid catalysts, such as tungstated zirconia, sulfonated poly(styrene/divinylbenzenes), and perfluorinated ion exchange resins, were tested in packed bed reactors and evaluated according to their turnover frequencies and selectivities to internal olefins. Branched products and oligomers are also made in

varying amounts. The more promising catalysts were evaluated under continuous flow until at or near deactivation. Used catalysts are being examined to determine the cause(s) of deactivation. Iron pentacarbonyl, a chain-walking catalyst, has been tested in a batch reactor in order to determine the optimal catalyst concentration, temperature, and residence time. Other chain walking catalysts will be tested, as will methods to re-activate the acid catalysts.

10. Rare Earth/Transition Metal Oxides for Tar Reforming

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Tar removal from syngas from biomass or coal/biomass gasifiers plays an important role in the overall process. Problems caused by tar buildup downstream, such as pipeline blockage and catalyst deactivation, are eliminated by converting tars to fuel gases. Rare earth oxides (REOs, e.g., Ce/LaO_x) mixed with transition metals (e.g., Mn, Fe) were synthesized by templated sol-gel or evaporation induced self assembly methods, or supported on thermally stable alumina. Cleanup reactions were in a range near that of a gasifier (873 - 1073 K) to enable better process heat integration, using synthetic syngas mixtures with C₁₀H₈ as a tar model compound with/without H₂S. Some commercial Ni reforming catalyst formulations were examined comparatively. Select fresh and used catalysts were characterized by BET, TPO, XRD, XANES. We found that some transition metal ions remain in the fluorite structure of CeO₂ but some are present as an amorphous nanocrystalline phase. Reforming is the primary reaction although trace amounts of C₃, C₆ were observed occasionally. The reforming activity without S is in the order: Ni/K/Mg/Al > Fe/REOs > Mn/REOs ~ REOs > La/Al > Mn/Al. But in the presence of H₂S, Fe/REOs showed the best resistance to sulfur poisoning or the reforming activity, while Ni15/K/Mg4/Al showed the least. While the water-gas shift activity was similar for most of these catalysts, the (undesirable) methanation activity was not: Fe/REOs < Mn/REOs < REOs < Ni2/Ca/Mg2/Al. Carbon deposition was found in partially deactivated catalysts and quantified by temperature programmed oxidation.

11. *In situ*-DRIFTS study of the Selective Catalytic Reduction of NO_x by NH₃ Over a Cu-Exchanged Small Pore Zeolite

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Nitrogen oxides, NO_x (NO+NO₂), are considered significant air pollutants. Selectively catalytic reduction of NO_x with NH₃ (NH₃-SCR) is a leading technology candidate for NO_x emissions control. Vanadia-based catalysts are used in NH₃-SCR in stationary application. However, it suffers from low activity and selectivity at high temperature. Transition metal exchanged zeolite frameworks with medium and large pores have also been considered potential candidates as SCR catalysts. However, their hydrothermal instability is problematic. Recently, the Cu-exchanged chabazite framework type zeolite with small pores, such as SAPO-34 and SSZ-13, has received a great deal of attention due to exceptional hydrothermal durability and enhanced SCR activity which enabled its commercial introduction in to on-highway diesel applications. The objective of this study is to investigate the intrinsic SCR reaction mechanism on Cu-exchanged SAPO-34 catalysts by using *in situ* DRIFTS coupled with a mass spectrometer to measure the inlet and outlet concentrations. The present work clearly shows that formation of surface nitrates and nitrites is the key step in NH₃-SCR over Cu-SAPO-34. These surface complexes readily react with surface NH₃ to form an NH₄NO₃ intermediate on the Lewis acid sites that can be easily reduced by NO to generate N₂. The NH₃ on Brønsted acid sites likely migrates to Lewis acid sites to provide more NH₃ for reaction.

12. Sulfur Poison Effects and Mechanism Study for NH_3 -SCR reaction over Cu-SAPO-34

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Sulfur poisoning is still a durability issue for base metal/zeolite selective catalytic reduction (SCR) catalysts used for abatement of NO_x . Most studies have been based on SO_2 . However, as diesel oxidation catalysts (DOCs) are employed upstream of the SCR catalyst, it is likely that some of the SO_2 is oxidized into SO_3 . Therefore, investigating the impact of SO_3 on Cu/zeolite SCR catalyst is critical.

In this study, we have investigated the poisoning effects of SO_2 and SO_3 and the poisoning mechanism over a Cu-SAPO-34 catalyst. Both SO_2 and SO_3 affected the NH_3 SCR activity over Cu-SAPO-34; SO_2 had less poisoning effect than SO_3 . The poisoning mechanisms of SO_2 and SO_3 on Cu-SAPO-34 for NH_3 -SCR were different. For SO_2 , it affected the low temperature activity of NH_3 SCR due to competitive adsorption of SO_2 with NO_x at low temperatures, while at higher temperature ($>300^\circ\text{C}$), it did not affect the activity because of desorption of SO_2 . For SO_3 , it affected the activity of SCR in the whole temperature range. This might due to SO_3 interacting with NH_3 and forming NH_4HSO_4 or $(\text{NH}_4)_2\text{SO}_4$, which deposited on the surface of the catalyst, hence blocking active sites. Both SO_2 and SO_3 poisoned catalysts could be recovered and almost 90% of its activity regained by exposure to air at 600°C ; also an even higher low temperature activity was obtained with a higher temperature exposure (735°C), probably due to the sample changing during the high temperature calcination.

13. Kinetic Study of the SO_2 Oxidation Reaction Over a $\text{Pt}/\text{Al}_2\text{O}_3$ Diesel Oxidation Catalyst

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Sulfur is a common poison for diesel oxidation catalysts. In order to understand the deactivation behavior of diesel oxidation catalysts (DOCs), as well as the sulfur species effect on downstream catalyst systems, i.e. selective catalytic reduction (SCR) and lean NO_x trap (LNT) catalysts, the SO_2 oxidation kinetics need to be understood. In this work, an SO_2 oxidation experimental study was performed and a kinetic model was developed and verified with the experimental data in order to properly describe SO_2 oxidation over $\text{Pt}/\text{Al}_2\text{O}_3$.

A monolith supported $\text{Pt}/\text{Al}_2\text{O}_3$ (50 g/ft³ Pt) catalyst was used in the experiments. A separate reactor upstream of the main reactor was used to generate SO_3 when SO_3 was required in the feed for the kinetic and deactivation studies. The outlet gas concentrations were measured using a MKS MultiGas 2000 FT-IR analyzer. The SO_2 oxidation rate dependencies on the SO_2 , O_2 and SO_3 concentrations were determined experimentally where the reactor was operated under a differential reactor regime. It was found that the SO_2 oxidation reaction was nearly first order with respect to SO_2 whereas the reaction orders of -0.24 and -0.42 were observed for O_2 and SO_3 , respectively. An activation energy of 95 kJ/mol was measured in the presence of SO_3 in the feed.

A reaction mechanism was proposed for the catalytic oxidation of SO_2 on $\text{Pt}/\text{Al}_2\text{O}_3$ and a kinetic model was developed based on this mechanism and our findings of the reaction orders. Some parameters were identified in the literature, but others had to be fit to match the experimental data. The relative importance of each step in the reaction mechanism was studied using the developed model.

14. A Computational Evaluation of Steady-State Bifunctional Catalysis

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The pioneering work by Nørskov and co-workers on the application of density functional theory (DFT), linear scaling relations and the resulting volcano curve in heterogeneous catalysis has made it possible to predict a pool of promising material candidates for various catalytic processes computationally [1–4]. However, as the

optimal catalysts are not always practical due to their high cost or insufficient long-term stability, it is essential to continue developing new and affordable materials with high catalytic activity. In the literature, several examples of high performance catalysts with multiple site-specific functionalities at steady-state have been reported [5–8]. The most common systems consist of two distinct sites that catalyze different reaction steps independently and are often referred as “bifunctional catalysts”. Using DFT and microkinetic modeling, we aim to understand the mechanisms that are responsible for bifunctional activity and provide a computational framework for screening of bifunctional catalysts. Our results indicate that there are theoretical limits for the achievable activity improvement and bifunctional catalysts do not necessarily outperform single-site catalysts. More specifically, for CO oxidation on bimetallic systems we found that the overall activity is not significantly altered when bifunctional catalysts are considered, but equally active bifunctional catalysts may be tailored from less active and cheaper components.

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15. Consequences of the Local Environment on the Activity of Brønsted Acid Sites in Zeolite Catalysis

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Efficient application of zeolite catalysts demands a systematic approach to identify factors influencing their overall performance. Although the effect of shape-selectivity in zeolite catalysis has been investigated, the influence of local environment on the intrinsic activity of Brønsted acid sites is not well understood. Most theoretical studies on MFI-type zeolite (HZSM-5), for instance, have focused on performance of only one location of active sites out of multiple possibilities in the zeolite framework. We used a computational method based on density functional theory (DFT) to rigorously investigate the differences in Brønsted acidity for all active sites located within zeolite pores (internal) and on the crystal surface (external). Here, we report the binding energies of four probe molecules to different active sites in three zeolite structures with different pore size and geometry to explore the effects of sorbate confinement. Investigations of ZSM-5 (MFI framework type) revealed a nonuniform performance of active sites suggesting unique differences in the activity of internal and external Brønsted acid sites. This study was extended to two other zeolite frameworks (GIS and RHO) with smaller pore apertures and varying degrees of pore volume (i.e. spatial confinement). Moreover, we discuss an experimental method to characterize the intrinsic activity of internal and external active sites using a surface passivation technique to create zeolite core-shell structures with an aluminosilicate (catalytically active) core and a purely siliceous (catalytically benign) external layer. Collectively, we seek to develop a synergistic methodology that combines DFT, novel synthesis, and catalytic testing to explore structure-function relationships in zeolite catalysis towards the development of rational approaches in catalyst design.

16. Synthesis and Catalytic Activity of Individual or Mixed Carbides of Group V and VI Transition Metals

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Transitions metal carbides are promising catalysts for demanding applications in heavy oil processing because they can withstand high temperatures and can exhibit properties similar to platinum while being much less costly. Some monometallic carbides, particularly those of molybdenum and tungsten, have been described in

the literature [1, 2] and have been successfully employed for hydrogenation and hydrotreating reactions. Here, we expand this class of catalysts by varying composition and structure. The synthesis and catalytic activity of mixed metal carbides of molybdenum and niobium with various metal ratios and of differently structured tungsten carbides have been investigated. Samples were prepared by carburization of oxide precursors in a mixture of $C_2H_6/H_2/Ar$. The formation of carbides was monitored by thermogravimetry with evolved gas analysis by online mass spectrometry. The carbide structures were verified by powder X-ray diffraction. Samples were characterized by N_2 physisorption with Brunauer–Emmett–Teller (BET) analysis, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The prepared carbides were passivated with various gases such as air or CO_2 to elucidate the role of passivation on reduction (or activation) temperature and catalytic activity. The catalytic activity of the carbides for hydrogenation of toluene was tested at a pressure of 30 bar and reaction temperatures of 250 and 300°C. The main product of the hydrogenation in all cases was methylcyclohexane. Results show that samples passivated by CO_2 are activated at a lower temperature and show a higher catalytic activity than those passivated in air.

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17. Study on the NO_x Storage Mechanisms and Sulfur Tolerance over NSR Catalyst Pt/K/TiO₂-ZrO₂

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The NO_x storage and reduction (NSR) technique proposed by Toyota provides a feasible approach to the abatement of lean-burn NO_x. In the present study, a series of NSR catalysts Pt/K/TiO₂-ZrO₂ were prepared by an impregnation method. The results of NO_x storage capacity (NSC) show that as the calcination temperature increases, the NO_x storage capacities of the catalysts show volcano-type tendency, with the maximum appearing at 800°C. The results of N_2 adsorption/desorption, XRD, TPD and *in-situ* DRIFTS show that the storage capacity is tightly related to the structures and chemical properties of the supports and the state of K species, regardless of the specific surface areas. The results of H_2 -TPR reveal that the reduction of the sulfates formed on Pt/K/TiO₂-ZrO₂ catalyst with the support calcined at 500°C started from about 200°C and completely finished before 500°C, which is about 200°C lower than that of traditional Pt/Ba/Al₂O₃, showing the good ability tolerant to sulfur.

In-situ DRIFTS was employed to determine the roles of individual catalyst components and to identify the adsorbing species at different temperatures. The results show that no adsorbed NO_x species were detected over TiO₂-ZrO₂, while nitrite and nitrate species could be identified simultaneously over K/TiO₂-ZrO₂. After Pt deposition, only nitrates species, such as free nitrate ions and monodentate or bidentate nitrates, were observed. The main NO_x storage route is via the potassium sites (I) adjacent to Pt, the potassium sites (II) away from Pt trap NO_x only after the saturation of potassium sites (I).

18. A Multiscale Approach to the Rational Design of Zeolite Catalysts

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The use of zeolite catalysts in areas such as biofuels and emission technologies in response to increasing energy demand and stringent environmental standards requires concerted efforts to improve zeolite performance. Here, we will present a multiscale approach to address this challenge using a versatile, facile synthesis technique employing zeolite growth modifiers (ZGMs) to tailor zeolite crystal size and habit. To this end, we utilize a synergistic combination of the following techniques: detailed atomistic simulations to examine ZGM

binding modes on individual crystal faces, force spectroscopy to assess ZGM-crystal interactions, atomic force microscopy to characterize the effects of ZGM on zeolite surface architecture, and bulk crystal characterization studies to quantify ZGM efficacy. These studies span multiple length scales (macroscopic to molecular) to identify fundamental mechanisms of growth modification. These studies are a platform for rational design wherein fundamental understanding of ZGM-crystal recognition and the judicious selection of modifiers can optimize zeolite catalysts.

19. Controlling Crystal Polymorphism in Organic-Free Syntheses of Na⁺-Zeolites

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The unique acidity, thermal stability, and shape-selectivity of nanoporous zeolites are utilized in industrial applications spanning catalysis to ion exchange. Difficulties in the formation of zeolites in organic-free synthesis are prevalent and the most common concern is the formation of undesirable crystal phase impurities. Oftentimes organic structure directing agents are used to form phase-pure crystals, though these additives can be costly and must be removed by post-synthesis calcination. In order to both understand and control organic-free polymorphism, we constructed ternary diagrams based on varying synthesis conditions using only Na⁺ cations as the structure directing agent. These kinetic phase diagrams revealed regions of pure and mixed phases of eight zeolite framework types synthesized from colloidal silica and sodium aluminate. Increasing temperature and/or crystallization time revealed phase transformations following the Ostwald rule of stages, wherein metastable structures dissolve and recrystallize into more thermodynamically stable structures. Moreover, it was found that water content substantially influences the phase diagrams by facilitating the formation of structures that usually require organics and/or dramatically reducing the synthesis temperature required to obtain higher density zeolite frameworks. The ternary diagrams developed in this study provide the basis for parameter selection to rationally design phase-pure zeolite catalysts and provide systemic insight into the combined effect of synthesis parameters on phase behavior and crystal properties.

20. Tuning Physicochemical Properties of Growth Modifiers to Regulate Zeolite Crystallization

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There is growing interest in zeolite science across a wide range of applications. Despite their extensive use, however, an understanding of their growth mechanism remains elusive. Here we will discuss the rational design of zeolite L crystals. We will discuss our studies of zeolite L crystallization in the presence of zeolite growth modifiers (ZGMs), which mediate anisotropic crystal growth through specific interactions with crystal faces. A library of modifiers ranging in length and functionality were investigated. Through the appropriate selection of ZGMs, zeolite L morphology can be markedly changed from high aspect ratio needle-like crystals to thin discs. ZGM hydrophobicity was found to be an effective molecular descriptor of its efficacy, while polymers proved to be more effective modifiers than their corresponding monomers. We will also discuss how atomic force microscopy was used to probe zeolite surfaces at the microscopic level, revealing unique surface features induced by ZGM-crystal interactions.

21. Bimetallic Hydroformylation Catalysis: The Role of Water and New Ligand Design

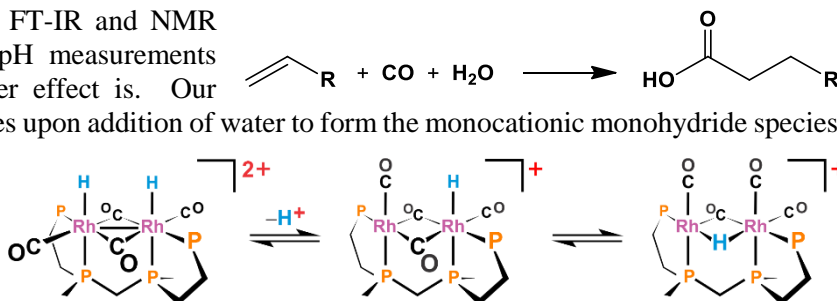
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Our bimetallic hydroformylation catalyst, $[\text{Rh}_2\text{H}_2(\mu\text{-CO})_2(\text{rac-et,ph-P4})]^{2+}$, performs much better when water is added to the acetone solvent. *In situ* FT-IR and NMR studies combined with some simple pH measurements have finally sorted out what the water effect is. Our dicationic dihydride catalyst deprotonates upon addition of water to form the monocationic monohydride species, $[\text{Rh}_2\text{H}(\mu\text{-CO})(\text{CO})_3(\text{rac-et,ph-P4})]^+$.

Hydroformylation results may also be presented on a new more strongly coordinating ligand system designed to limit catalyst fragmentation reactions.



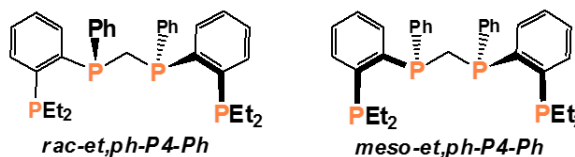
22. Synthesis and Characterization of a New Binucleating Tetraphosphine Ligand for Catalytic Applications

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A new binucleating tetraphosphine ligand has been synthesized, separated, and fully characterized. The current dirhodium hydroformylation catalyst system based on our original tetraphosphine ligand shown in the previous abstract suffers from serious fragmentation reactions that lead to loss of bimetallic cooperativity and catalysis. The new P4 ligand system has been characterized by NMR,

high resolution mass spectroscopy, and a number of nickel crystal structures. The transition metal chemistry so far supports the far stronger chelate effect in this ligand for coordinating metal centers. A variety of catalytic studies are underway using bimetallic complexes based on this new P4 ligand.



23. Mitigating Nitrate/nitrite Water Emissions Through Bimetal-catalyzed Reduction

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Nitrate (NO_3^-) is often found in the groundwater and surface water in the United States, especially in agricultural areas intensively using nitrate rich fertilizers. It is widespread due to its high stability and solubility. The consumption of nitrates and its transformation production—nitrite (NO_2^-) would cause a series of adverse health effects, including methemoglobinemia or blue baby syndrome. The catalytic reduction of nitrate/nitrite has received intense research interests since Pd based catalysts (e.g. Pd-Cu, Pd-In and Pd-Sn) can convert nitrate/nitrite to harmless nitrogen (N_2) with reducing agent hydrogen. However, due to the over-reduction, ammonia (NH_3) was also easily formed besides nitrogen. In the view of water treatment, high selectivity to nitrogen is preferred since ammonia is still contaminant in water. In our study, we demonstrates the application of Pd-on-Au NP catalysts on the reduction of nitrite, a common groundwater contaminant. Pd-on-Au NPs exhibited a “volcano-shape” dependence of activity on Pd surface coverage. 80 sc% Pd-on-Au NPs reached the maximum activity, which had a rate 15× and 7.5× times greater than pure Pd NPs (~4 nm) and traditional Pd/ Al_2O_3 catalyst. In addition to the higher activity, Pd-on-Au NPs also showed a nearly 100% selectivity to N_2 over toxic ammonia and good deactivation resistance to chlorides. These Pd-on-Au NPs may be widely used for highly active and selective reduction of oxyanions such as ClO_4^- , BrO_3^- and NO_3^- in groundwater treatment applications after modified with “promoter” metals like Re, Cu, In and Sn.

24. Hydrogen Generation from Formic Acid at Room Temperature Using Pd-on-Au Catalysts

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Increasing interest has been attracted to formic acid (HCOOH, FA) as a potential source for *in situ* H₂ generation for fuel cells and hydrogenation reactions due to its feasibility in transportation and safety in handling in aqueous form. FA can decompose *via* dehydrogenation (to H₂ + CO₂) and *via* dehydration (to CO + H₂O). Dehydrogenation is desired to produce continuous and stable H₂ flow at near-ambient conditions whereas dehydration should be minimized. Despite some recent progress, few results have been reported on the room temperature dehydrogenation of FA using solid catalysts. We designed palladium-on-gold nanoparticles (Pd-on-Au NPs) precisely as 4 nm Au core with atomic layer thin Pd coatings corresponding to various Pd surface coverages (sc%) as confirmed by X-ray absorption spectroscopy. Our recent kinetic results have showed that carbon supported Pd-on-Au NPs with multi-layer Pd surface coverage (300 sc% Pd-on-Au/C) was highly active for FA decomposition at room temperature. The catalyst had a calculated H₂ generation rate of 137 mL/g_{Pd}/min and an initial TOF of 123 h⁻¹ based on 10 min's data, much more active than its monometallic Au/C (not active) and Pd/C (TOF = 38 h⁻¹). The reaction rate was in the range of homogenous catalysts with no evidence of CO formation. Through adjusting Pd surface coverage and Au core size, the catalytic activity and selectivity could be further modulated.

25. Reductive Photocatalysis Using *In-situ* Generated Hydrogen

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We develop a bifunctional semiconductor-metal composite material that functions as a reduction photocatalyst using *in-situ* generated hydrogen (H₂). The Pd-on-Au/TiO₂ (0.1wt% Pd, 1wt% Au) catalyst was synthesized by reducing dihydrogen tetrachloropalladate (II) onto a commercially available Au/TiO₂ catalyst. As the test reaction, the hydrodechlorination of trichloroethene (TCE, a common groundwater contaminant) was observed to occur in batch reactor studies, under both aerated and deaerated conditions upon illumination with a 400 W xenon light source. Analysis of the reactor headspace confirmed that reductive hydrodechlorination products are formed. No photocatalytic TCE oxidation is observed. Control experiments without TCE reveal that *in-situ* H₂ is generated by photocatalytic water splitting, irrespective of the presence of air. We therefore infer that the Pd-on-Au/TiO₂ simultaneously photocatalyzed water splitting and catalyzed reductive TCE hydrodechlorination in the same batch reactor. Extension of this study to other bifunctional semiconductor-metal systems and groundwater contaminants could significantly simplify future remediation efforts.

26. Aqueous Phase Hydrodechlorination Over Au/Al₂O₃

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Nano-gold catalysts have demonstrated high activity to oxidize CO at low temperatures. Previous works from our group demonstrated the enhancement provided by gold in the bimetallic Pd-Au catalyst for the hydrodechlorination of trichloroethylene. In this study, we explore the hydrodechlorination reaction of chloroform and trichloroethylene over alumina-supported gold nanoparticles. A commercially available Au/Al₂O₃ (1.2 wt% Au) catalyst was obtained and calcined at different temperatures to study the effect of size on the catalytic activity. Analysis of the reactor headspace confirmed full dechlorination, resulting in

hydrocarbon products with chain lengths ranging from 1 to 4 carbon. Evidence of hydrocarbon polymerization is presented. These results highlight the hydrodechlorination ability of gold nanoparticles at room temperature, atmospheric pressure, in DI water, and in the presence of H₂ gas.

27. Reaction of Acetone on Rutile TiO₂ (110)-1x1 Surface with Oxygen Adatom

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Using scanning tunneling microscopy (STM), we studied the reaction of acetone on the oxidized rutile TiO₂ (110)-1x1 surface with oxygen adatom (O_a). The STM experiment results show that the acetone molecules preferably adsorb at the bridge-bonded oxygen (O_b) vacancy (V_O) sites. They either move along the O_b row or diffuse from V_O to the five-fold coordinated Ti⁴⁺ row and then move along the Ti⁴⁺ row. With an O_a located one lattice distance away on the neighboring Ti⁴⁺ row, the acetone molecule on the V_O site can react with the O_a and form the stable acetone-V_O-O_a complex. When the mobile acetone molecule diffuses along the Ti⁴⁺ row, it reacts with the O_a, forming the Ti-bound acetone-O_a complex. The sequential isothermal STM images taken at 300 K show that the Ti-bound acetone-O_a complex is not stable. It dissociates back to an O_a and an acetone which continues to diffuse. The process assists the diffusion of surface O_a by exchanging the acetone oxygen with O_a.



A Brief History of the Southwest Catalysis Society

As recounted by **Joe W. Hightower**, Professor Emeritus, Rice University (April 2009)
B.S. '59 - Harding University; M.S. '61 and Ph.D. '63 - The Johns Hopkins University

I came to Rice University from the Mellon Institute in Pittsburgh during the summer of 1967 and immediately set out to meet catalyst people in the area. We announced an organizational meeting to be held at Rice, **Fall 1967**. There were 63 people as charter members of what was to become the Southwest Catalysis Club. Jim Richardson (Esso Research and Engineering, now University of Houston) drafted the Bylaws and was elected Vice President, Jack Lunsford (Texas A&M University) was Secretary, Paul Conn (Shell Oil) was the Treasurer, and I served as the first elected President. The officers held the first all-day Spring Symposium in May 1968 in the Grand Hall at Rice, and the SWCS was off and running (42 years and counting!). [As a note, I did my PhD thesis research with **Professor Paul Emmett** at Johns Hopkins, which involved isotopic tracer studies of secondary reactions that occur during catalytic cracking of petroleum products.]

At the time we started, there were about half a dozen "Catalysis Clubs" scattered around the country: Chicago, Pittsburgh, New York, Philadelphia, California, and perhaps one more. I knew people in all these "Clubs" though groups like the Gordon Research Conferences on Catalysis, and they all encouraged us to start a club in the SW. **Why 5 states?** Texas was obvious. Arkansas was included because of Sam Siegel (Chemist at UArk); Louisiana, because of several researchers at Esso in Baton Rouge; Oklahoma, because of several Phillips researchers in Bartlesville; and New Mexico, because of people at University of New Mexico and at Sandia National Labs in Albuquerque. In spite of the long distances, people from all these places attended some of the early meetings held twice a year, which sometimes had attendance near 200. Most of the early meetings were held at Rice or in the Auditorium at the Shell-Westhollow labs. In later years, the meeting was held in nearby places like Austin, College Station, and New Orleans.

What was going on that made the late 60s an optimal time to establish the SWCS? I think the biggest factor was Shell downsizing its labs in Emeryville, CA and moving most its catalysis people to a new research facility at Westhollow. At the same time, Esso was increasing its applied catalysis work both in Baytown 30 miles east of the city and in Baton Rouge. For several years, Phillips Petroleum had been accumulating an amazing number of patents in catalysis at their laboratories in Bartlesville. Bob Eischens came from New York and was applying his pioneering infrared studies at Texaco in Port Arthur. Celanese had several catalysis people doing research near Corpus Christi. Many of you may recall that Texas City was devastated by the largest US chemical plant explosion of an ammonium nitrate ship in the mid-40s. After the explosion, Monsanto rebuilt its facilities there, where workers were doing research on improving catalytic processes for styrene and acrylonitrile manufacture. Petrotex Chemical in Pasadena, another suburb on Houston's ship channel, was optimizing its butadiene and C₄ olefins production through catalytic processes.

In addition, catalysis groups were springing up at several universities, including surface science by the late John Mike White at the University of Texas, Jack Lunsford's and Wayne Goodman's highly productive groups at Texas A&M, Richard Gonzales at Tulane, Jim Richardson at U of H, Kerry Dooley at LSU, Tom Leland and me at Rice, and groups at other universities in the 5-state area. What was lacking? There was no formal mechanism for these diverse groups to exchange information or get advice in the southwest. The time was ripe for an organization where catalysis could be openly discussed. Although much catalysis research is proprietary, enough was sufficiently open to create a stimulating environment for sharing mutual interests, many focusing on new ultra-high vacuum analytical equipment that was being rapidly developed.



The first thing we did was to organize an NSF-supported workshop at Rice which (not surprisingly) concluded that more funding was needed for research on catalysts for fuels, environmental protection (cat converters), chemicals, etc. At that time, demand was also great for new employees with catalysis training, but the supply was quite limited. This provided an occasion for the development of short courses to train industrial employees in heterogeneous catalysis. Several courses were started around the country. One of the most successful was started at Rice and has continued for more than 30 years through the University of Houston. It can be said, then, that **SWCS was instrumental in starting these heterogeneous catalysis short courses.**

The "Club" was soon invited to join the other half dozen Clubs as a part of the growing North American Catalysis Society. Being the new kid on the block, our Club was asked to host its first biennial North American Meeting (NAM-2) in February 1971, which was held at the Astrodome Hotel in Houston. Jim Richardson and I were Associate and General Chair of the meeting, while Paul Venuto (Mobil Research/Development and a colleague of the late Heinz Heinemann) was in charge of the Program. At that meeting the late Dr. R. J. Kokes (one of my professors at Johns Hopkins) and Dr. H. S. Bloch (Universal Oil Products) were recipients, respectively, of the first Paul H. Emmett and Eugene J. Houdry Awards in fundamental and applied catalysis.

In 1985, the Southwest Catalysis Society was again called on to host a five-day 9th North American Meeting (NAM-9) at Houston's Adam's Mark Hotel. This time, Jack Lunsford and Lynn Slaugh were General and Vice Chair; I was Technical Program Chair. Most recently, the SWCS members organized the spectacular North American Meeting at Houston's downtown Hilton Americas Hotel in 2007, attended by over 1000 delegates from all over the world, "Celebrating Catalysis Texas Style." Kudos again to SWCS officers Kerry Dooley, Brendan Murray, Scott Mitchell, Michael Reynolds, Yun-Feng Chang, Michael Wong, and many, many others! **All told, the SWCS has hosted 3 national events now: 1971 (NAM-2), 1985 (NAM-9) and 2007 (NAM-20).**

Rice University Map (<http://www.rice.edu/maps/maps.html>)

RICE UNIVERSITY CAMPUS MAP



Building numbers

43: Grand Hall – Ley Student Center (meeting site)

61: Rice Memorial Center (on-your-own lunch)

51: Central Campus Garage (ample visitor parking)