

# SouthWest Catalysis Society 2011 Spring Symposium



**April 15, 2011**

**BioScience Research Collaborative Building  
Rice University – Houston, TX**

**A Special Thank You to Our Sponsors!**





#### Chair

Michael A. Reynolds  
Shell Oil Company  
Houston, TX 77082  
[mike.reynolds@shell.com](mailto:mike.reynolds@shell.com)

#### Chair-Elect

George Stanley  
LSU, Chemistry Dept.  
232 Choppin Hall  
Baton Rouge, LA 70803-1804  
[gstanley@lsu.edu](mailto:gstanley@lsu.edu)

#### Secretary

Andy Moreland  
Valero Energy Corporation  
San Antonio, TX  
210-345-2067  
[andrew.moreland@valero.com](mailto:andrew.moreland@valero.com)

#### Treasurer

John W. Novak, Jr.  
BASF Catalysts, LLC  
Baton Rouge, LA, 70817  
[john.novak@basf.com](mailto:john.novak@basf.com)

#### Directors

Bert Chandler  
Trinity University  
Department of Chemistry  
San Antonio, TX 78212  
210-999-7557

Scott Mitchell  
SABIC Americas  
Sugarland, TX 77478  
[scott.mitchell@sabicus.com](mailto:scott.mitchell@sabicus.com)

Lin Luo  
The Dow Chemical Co.  
2301 Brazosport Blvd.  
Freeport, TX 77541  
[LLuo2@dow.com](mailto:LLuo2@dow.com)

#### Past-Chair

Michael S. Wong  
Rice University  
Chem. Biomolecular Eng.  
MS-362  
Houston, TX 77251-1892  
713-348-3511  
[mswong@rice.edu](mailto:mswong@rice.edu)

#### NACS Representative

Brendan Murray  
Shell Global Solutions  
Houston, TX  
[brendan.murray@shell.com](mailto:brendan.murray@shell.com)

Dear Members:

The SWCS Officers and I would like to welcome all of you to the 2011 Spring Symposium here at Rice University this **Friday, April 15, 2011**.

It is our privilege to present 9 distinguished speakers and several talented students who will present posters. This year the SWCS officers have collaborated with Professor Michael Rosynek and Professor Wayne Goodman of Texas A&M University to co-sponsor a symposium honoring Prof. Jack Lunsford for his accomplishments in teaching and in the field of catalysis. Additionally, the Society is proud to present the inaugural *SWCS Award for Excellence in Applied Catalysis* later in the day.

On-site registration will begin at 7:30 AM and the program will begin at 8:00 AM. The **registration fee is \$50**, which includes NACS & SWCS yearly membership dues, several coffee breaks and a box lunch. To speed registration, please bring your business card along with your registration fee. **Students pay \$10** for registration. Unfortunately, we cannot take credit cards for payment. For those of you who have colleagues that cannot attend, please ask them to mail in membership dues (\$25) to our Treasurer, Dr. John Novak.

Regarding the poster session, students should direct their questions to Dr. Lin Luo who is this year's poster Chair. Meritorious cash prizes will be given to students or post-docs for the best posters. Only the presenting author of each poster will qualify. Poster boards (4' x 6') and easels will be provided at the site. Please try to set your posters up before lunch.

We hope you will enjoy the meeting, and please feel free to introduce yourself to the SWCS Officers and each other.

Cheers!

Michael A. Reynolds, Chair



## **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.



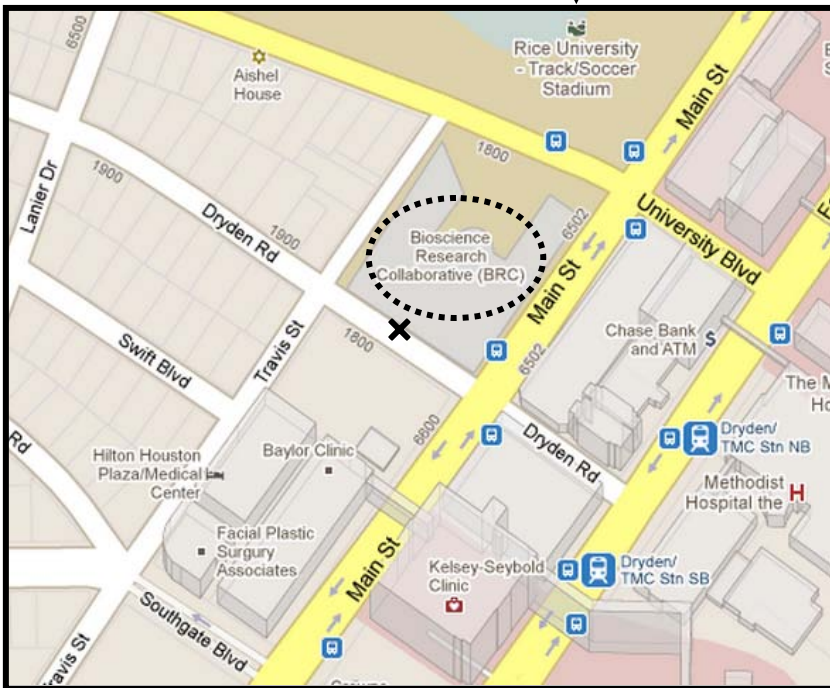
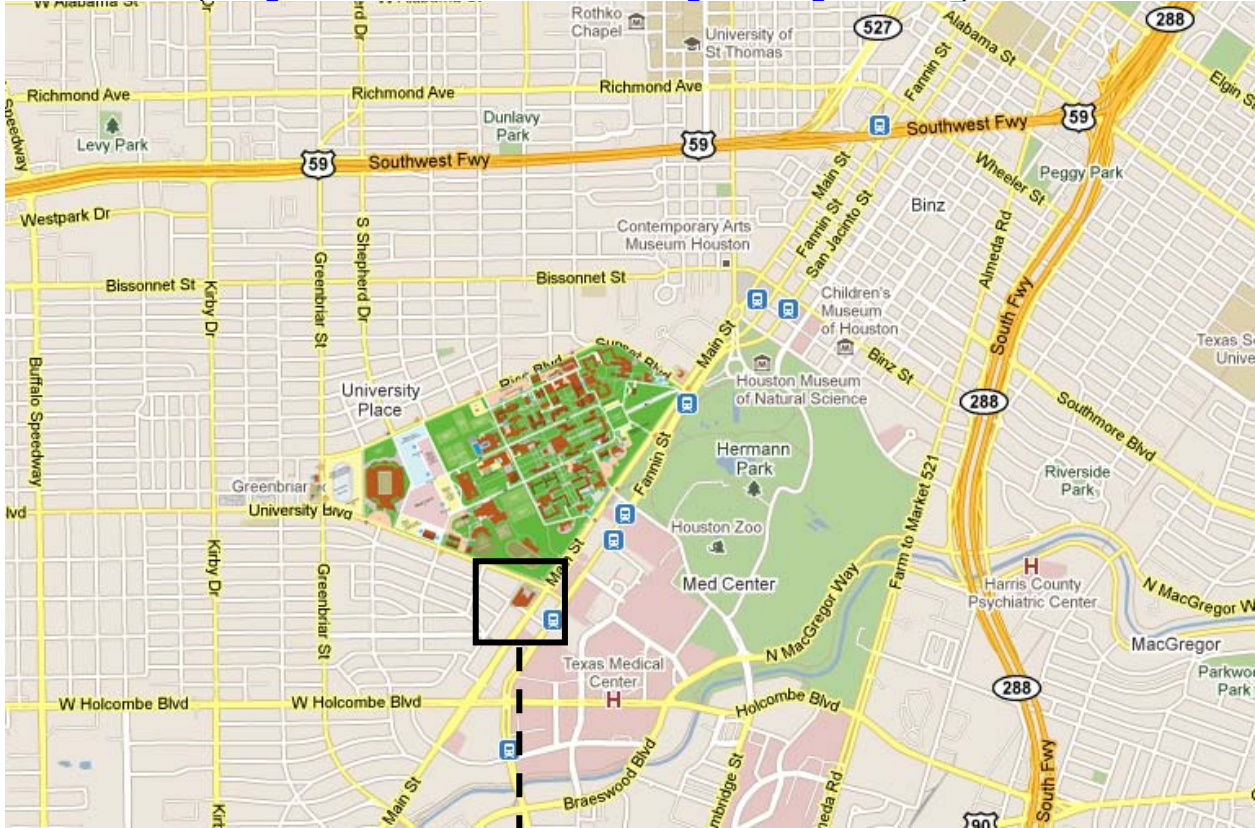
In addition, catalysis groups were springing up at several universities, including surface science by the late John Mike White at the University of Texas, Jack Lunsford's and Wayne Goodman's highly productive groups at Texas A&M, Richard Gonzales at Tulane, Jim Richardson at U of H, Kerry Dooley at LSU, 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>



**Meeting Site**  
 BioScience Research Collaborative (BRC)  
 6500 Main St.  
 Houston, TX 77005

"x" marks entrance to underground parking – use your credit card to pass through the gate



## TECHNICAL PROGRAM

- 7:30 AM Registration – John Novak, Treasurer**  
BioScience Research Collaborative Building
- 8:00 AM Welcoming Remarks – Michael Reynolds, Chair**  
Auditorium
- 8:05 AM Dr. Todd Ballinger (Johnson-Matthey; Wayne, PA)**  
“Functionality of Zeolite Containing Automotive Catalysts”.
- 8:35 AM Prof. Peter Stair (Northwestern University; Evanston, IL.)**  
"Catalyst Synthesis by Atomic Layer Deposition"
- 9:05 AM Prof. Abhaya Datye (University of New Mexico; Albuquerque, NM)**  
“Stabilization of Pd sintering on La-stabilized gamma-alumina”
- 9:35 AM Coffee Break / Poster Setup**
- 10:00 PM Prof. Bruce Gates (University of California-Davis; Davis, CA)**  
“Supported Metal Complexes and Clusters: Tuning Structures to Control Catalyst Selectivity”
- 10:30 AM 2010 NACS Ciapetta Lecture: Dr. Jeff Miller (Argonne National Lab, IL)**  
“Determination of CO, H<sub>2</sub> and H<sub>2</sub>O Coverage by XANES on Pt and Au During Water Gas Shift Reaction: Experiment and DFT Modeling”
- 11:15 AM SWCS Award for Excellence in Applied Catalysis Presentation**  
SWCS Officers will announce the inaugural recipient.
- 11:30 AM Lunch Break (on your own) / Poster Preview**  
tba
- ~12:10 PM Re-assemble**
- 12:15 PM Prof. Jack Lunsford (Texas A&M University; College Station, TX)**  
“A Peek into a Black Box: A Brief Review of Research in the Lunsford Group”
- 1:15 PM Dr. Shuibo (Steve) Xie (Chevron Corporation; Richmond, CA)**  
“Study of Renewable Diesel Production via Hydroprocessing Vegetable Oils”.
- 1:45 PM Professor Bert Weckhuysen (University of Utrecht; The Netherlands)**  
“In-situ Characterization of Fe-based Fischer-Tropsch Catalysts”



- 2:15 PM**     **Dr. Gerhardt Mestl (Süd-Chemie AG; Bruckmühl, Germany)**  
"Development of Selective Oxidation Catalysts at Süd-Chemie"
- 2:45 PM**     **Poster Session / Coffee Break**
- 4:15 PM**     **Poster Awards and SWCS Business**
- 4:45 PM**     **Adjourn**



## **Functionality of Zeolite Containing Automotive Catalysts**

Todd Ballinger  
Johnson-Matthey

Zeolites are used in automotive catalysts to function as hydrocarbon traps for gasoline engines and as selective reduction catalysts (SCR) for diesel engines. Hydrothermal stability of zeolites is necessary in order for the catalysts to meet emission regulations for 120,000+ miles. Active sites within zeolites have been identified for both hydrocarbon trapping and SCR catalysts, and research conducted to improve the hydrothermal stability of these sites has led to improved automotive catalysts.

## **Catalyst Synthesis by Atomic Layer Deposition**

Peter C. Stair

Professor of Chemistry, Department of Chemistry  
Northwestern University

Atomic Layer Deposition (ALD) has enormous potential for the synthesis of advanced heterogeneous catalysts with control of composition and structure at the atomic scale. The ability of ALD to produce conformal oxide coatings on porous, high-surface area materials can provide completely new types of catalyst supports. At the same time ALD can achieve highly uniform catalytically active metal and oxide phases with (sub-) nanometer dimensions.

Vanadium oxide species supported on high surface area oxides are among the most important catalytic materials for the selective, oxidative conversion of hydrocarbons to useful chemicals. In our laboratory ALD has been used to synthesize both the catalytic vanadium oxide and the supporting oxide on both high surface powders and anodic aluminum oxide (AAO) nanoliths. These materials have been characterized by SEM, XRF, ICP, UV-Vis absorption spectroscopy, Raman spectroscopy and evaluated for the oxidative dehydrogenation (ODH) of cyclohexane. More recently we have studied the synthesis of supported metal particles and developed what we call "ABC-type" ALD in which metal nanoparticles and support materials are grown sequentially in each ALD cycle. This method makes possible the synthesis exceptionally small particles, ca. 0.5 nm. Using additional ALD support layers at the conclusion of the growth, the metal particles can be stabilized against sintering while still remaining active at high temperatures and reaction conditions.





## **Stabilization of Pd sintering on La-stabilized gamma-alumina**

Abhaya K. Datye

*Center for Microengineered Materials & Department of Chemical & Nuclear Engineering  
University of New Mexico, Albuquerque, New Mexico 87131 (USA)*

The role of La in stabilizing  $\gamma$ -alumina and preserving high surface areas is well known. In this work, we report on another aspect of La: how it helps improve the dispersion of the metal phase. We have characterized Pd supported on La-stabilized  $\gamma$ -alumina, and observed that Pd particle size estimates made using average Pd-Pd coordination numbers obtained from analysis of Pd K-edge x-ray absorption fine structure (EXAFS) are consistently smaller than those obtained from high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and x-ray diffraction (XRD). Size determination using HAADF-STEM and XRD has practical lower detection limits of approximately 1 nm. Because the EXAFS practical lower limit is 1 atom in size, the smaller sizes obtained from EXAFS imply the existence of a large population of sub-nanometer-sized Pd.

Analyses of the scattering intensities in ACEM images are consistent with the presence of La-Pd dimers, Pd-Pd dimers, Pd-La-Pd trimers, as well as single atoms of La and Pd. Calculations based on density functional theory (DFT) show that these configurations are all energetically favorable. These results suggest that La atoms present on the surface of  $\gamma$ -alumina could serve as traps for diffusing Pd atoms, similar to the role played by BaO described in previous work, helping to slow Pd-metal particle growth, as well as preventing surface area loss via the formation of  $\gamma$ -alumina.

This work helps to elucidate the role of La in improving the dispersion of Pd on stabilized gamma alumina. These Pd/support interactions are of fundamental interest to understanding the stabilization of automotive catalysts.



## **Supported Metal Complexes and Clusters: Tuning Structures to Control Catalyst Selectivity**

Bruce C. Gates

Department of Chemical Engineering and Materials Science  
University of California, Davis

Supported metal complexes and metal clusters have been prepared on solid supports from precursors that react precisely with structurally well-defined surface sites. The resulting samples include those with uniform site-isolated catalytic sites that have virtually molecular structures and allow precise determination of catalyst structure-property relationships. With complementary spectroscopic methods, these species have been characterized in the functioning state and as they undergo structural changes. This presentation is a summary of oxide- and zeolite-supported metal catalysts synthesized from precursors incorporating reactive organic ligands and primarily on supports (MgO and zeolites) that provide relatively uniform sets of binding sites for the supported species. The characterization methods include IR, NMR, and X-ray absorption spectroscopies; scanning transmission electron microscopy (STEM); and density functional theory. The characterization results determine the number of metal atoms in the supported species, the bonding of the metals to the supports, identification of intermediates bonded to the metals, and in some cases reactive intermediates formed during catalysis.

Results are presented for supported single-metal-atom complexes and clusters of rhodium, osmium, and iridium. For example, complexes of iridium bonded to dealuminated HY zeolite were prepared from the precursor  $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ , giving supported  $\text{Ir}(\text{C}_2\text{H}_4)_2$  complexes in which each Ir atom is bonded to two oxygen atoms of the zeolite. These complexes were imaged by aberration-corrected STEM. They were converted reversibly into clusters approximated as  $\text{Ir}_4$ , and the changes were followed spectroscopically; the data indicate how the catalyst structure can be tuned by choice of the reactant composition. STEM has also been used to locate metals in the zeolite and to determine the precise atom-resolved structures of clusters on MgO. Similar results were obtained with HY zeolite-supported  $\text{Rh}(\text{C}_2\text{H}_4)_2$  complexes, which were reversibly converted into extremely small rhodium clusters, and the switch led to a dramatic shift in the performance of the catalyst from one highly selective for dimerization of ethylene to one highly selective for hydrogenation of ethylene.



## Determination of CO, H<sub>2</sub> and H<sub>2</sub>O Coverage by XANES on Pt and Au During Water Gas Shift Reaction: Experiment and DFT Modeling

*Jeff Miller*

Argonne National Laboratory, Chemical Sciences and Engineering Division

### ABSTRACT

**Water Gas Shift Reaction:** The turn-over-rate (TOR) for the water gas shift (WGS) reaction of 1.4 nm Au/Al<sub>2</sub>O<sub>3</sub> is approximately 20 times higher than that of 1.6 nm Pt/Al<sub>2</sub>O<sub>3</sub>. In addition, Au has high activity at lower reaction temperature than Pt. Operando XAFS experiments at both the Au and Pt L<sub>3</sub> edges reveal that under reaction conditions, the catalysts are fully metallic. Adsorption of CO, H<sub>2</sub> and H<sub>2</sub>O leads to changes in the XANES spectra that can be used to determine the surface coverage of each adsorbate under reaction conditions. During WGS, the coverage of CO, H<sub>2</sub>O, and H<sub>2</sub> are obtained by the linear combination fitting of the difference XANES, or  $\Delta$ XANES, spectra. Pt catalysts adsorb CO, H<sub>2</sub>, and H<sub>2</sub>O more strongly than the Au, in agreement with the lower CO reaction order. At low reaction temperature, the low rate of Pt is due to saturation of the metallic surface by adsorbed CO, while on Au there is little CO coverage and higher rates.

**Density Functional Theory of XANES Spectra:** In order to better understand these changes in XANES spectra with adsorbates and particle size, Pt nano-particles from about 1 to 10 nm have been prepared on different supports. The EXAFS spectra of the reduced catalysts in He show a contraction of the Pt-Pt bond distance as particle size is decreased below 3 nm. The bond length decreased as much as 0.13 Å for 1 nm Pt particles. Adsorption of CO and H<sub>2</sub> lead to a increase in Pt-Pt bond distance to that near Pt foil, e.g., 2.77 Å. In addition to changes in the Pt bond distance with size, as the particle size decreases below about 5 nm there is a shift in the XANES to higher energy at the L<sub>3</sub> edge, a decrease in intensity near the edge and an increase in intensity beyond the edge. At the L<sub>2</sub> edge, there are only small shifts to higher energy at the edge. However, beyond the edge, there are large increases in intensity with decreasing particle size. At the L<sub>1</sub> edge there are no changes in position or shape of the XANES spectra. Adsorption of CO and H<sub>2</sub> also lead to changes in the L<sub>3</sub> and L<sub>2</sub> edges, however, no changes are observed at the L<sub>1</sub> edge. Density Functional Theory and XANES calculations show that the trends in the experimental XANES can be explained in terms of the d electron density of states available near the Fermi level.



## **A Peek into a Black Box: A Brief Review of Research in the Lunsford Group**

Jack Lunsford  
Texas A&M University

Over the past four decades several types of spectroscopy have been effectively used to elucidate active sites and intermediates in catalytic reactions. Among these are electron spin resonance, laser induced fluorescence, and laser Raman spectroscopies. Each type of spectroscopy is limited in scope and unique in the information that can be revealed; yet, when appropriately applied the secrets of catalysis can be probed at a very elementary level.

## **Study of Renewable Diesel Production via Hydroprocessing Vegetable Oils**

Steve Xie  
Chevron Corporation

Diesel of  $-15^{\circ}\text{C}$  cloud point meeting ASTM D 975 ULSD specifications can be produced by hydrotreating canola oil and palm oil followed by a dewaxing step, with ~87 vol% yield of 350-650°F+ cut at 1,000 psig and  $1\text{ hr}^{-1}$  LHSV. While hydrodeoxygenation is the predominant reaction pathway of hydrocarbons formation from the dissociation of triglycerides, the relative contribution of decarboxylation pathway to the overall reaction scheme increases with decreasing pressure and increasing temperature. The catalyst lost at least 20°F activity after 2,000 hours on stream, and rejuvenation by injecting DMDS into feed stream to re-sulfide the catalyst can recover some but not all lost activity.



## **In-situ Characterization of Fe-based Fischer-Tropsch Catalysts**

Bert Weckhuysen  
University of Utrecht

An increasing demand for clean fuels and chemicals are expected to lead to an important shift from crude oil to natural gas as well as bio-feed as feedstock for chemical industries. This will certainly involve the use of Fischer-Tropsch (FT) technology, in which high molecular weight hydrocarbons are synthesized by catalytic hydrogenation of CO using cobalt- or iron-based Fischer-Tropsch catalysts. These GTL and BTL (Gas-to-liquid and Biofeed-to-liquid) processes currently deserve a lot of attention both in academia and chemical industries and as a consequence a lot of research is focusing on the development of improved catalyst compositions and understanding their behavior. In this lecture, two novel characterization approaches will be discussed to elucidate in more detail the catalyst phase changes occurring during FT catalysis. These methods involve in-situ Scanning Transmission X-ray Microscopy (STXM) and combined in-situ XAFS/XRD/Raman spectroscopy. The iron oxide-iron carbide phase transformations will be explained in terms of the chemical potential of carbon as a function of reaction temperature, pressure and gas feed composition.



## POSTER ABSTRACTS

### 1. Improved Olefin Isomerization Catalysts

James Bruno and Kerry Dooley

Louisiana St. Univ., Dept. of Chemical Engineering  
[jbruno8@tigers.lsu.edu](mailto:jbruno8@tigers.lsu.edu) (James Bruno)

The double-bond (terminal to internal) olefin isomerization reaction is surprisingly difficult for the higher C16-C20 olefins. One way to obtain high conversions to the internal olefins without positional isomerization is to use Pd-based catalysts for lower olefin conversions, and supported Nafion in series to obtain higher conversions. Problems with the Pd-based catalysts include activation, regeneration and susceptibility to poisons such as peroxides. Problems with the Nafion catalysts include poor crush strength and insufficient conversion to the more "internal" olefins. In this project we explore the factors which control and determine the behavior of these two catalyst types and how their lives can be extended. In particular, supports for Nafion other than silica are being examined.

### 2. Characterization and Catalytic Abatement of Alternative Diesel Fuel Emissions Using a Benchtop Engine System

Gregory S. Bugosh, Rachel L. Muncrief, Michael P. Harold

Department of Chemical and Biomolecular Engineering, University of Houston, Houston, TX

Diesel fueled, compression ignition engines generally have higher efficiency, increased durability, and more torque than their gasoline powered spark ignition counterparts. This has led to their use in most heavy duty vehicles for transportation and construction, and an increasing presence in passenger vehicles. The emissions from diesel engines contribute to pollution problems, especially in urban areas. Vehicle replacement or retrofit to reduce harmful emissions can be prohibitively expensive. Another option is to change the fuel type. In this study we evaluate the emissions of several types of alternative diesel fuel, including biodiesel made from various feedstocks (soy, canola, palm, tallow) and a gas-to-liquids (GTL) diesel. We utilize a single cylinder, diesel-powered, 5kW back-up electricity generator and analyze the exhaust using FTIR. The amount of carbon monoxide (CO), nitrogen oxides (NO<sub>x</sub>), and unburned hydrocarbons (HC) change depending on the fuel source and also the engine load. The composition of the exhaust can impact the effectiveness of catalysts to eliminate the harmful exhaust species. For example, reducing the CO concentration leads to lower light-off temperature and results in fewer cold start emissions. Real and simulated exhaust is passed over catalyst samples at specific temperatures and space velocities.

### 3. Study of Ammonia Formation Mechanism on Pt-Ba/Al<sub>2</sub>O<sub>3</sub> Monolith Catalyst in the Presence of NO, CO and Excess H<sub>2</sub>O

Prasanna R. Dasari, Rachel Muncrief, and Michael P. Harold

Dept. of Chemical & Biomolecular Engineering, University of Houston, Houston, TX 77204-4004 (USA)

Ground level ozone produced by the NO<sub>x</sub> emitted from lean burn and diesel engines is the main driving force for the active research in lean NO<sub>x</sub> reduction. Several NO<sub>x</sub> reduction technologies, such as selective catalytic reduction (SCR) using urea, lean NO<sub>x</sub> traps (LNT), combined LNT-SCR system etc., and are under development. The LNT-SCR technology utilizes NH<sub>3</sub> produced during the regeneration of the LNT in the downstream SCR. It is therefore, important to understand the NH<sub>3</sub> formation chemistry and kinetics on the LNT catalyst to develop an optimal

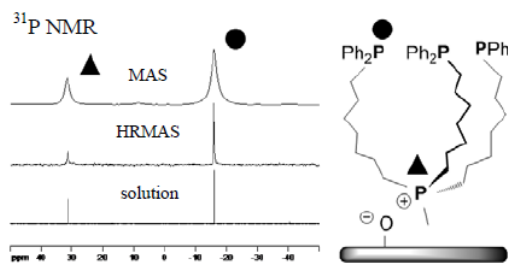
design and operating strategy for the LNT-SCR system. The production of  $\text{NH}_3$  is known to occur by reaction between  $\text{NO}$  and  $\text{H}_2$  under the rich conditions on precious group metals. However, in the presence of  $\text{NO}$ ,  $\text{CO}$  and excess  $\text{H}_2\text{O}$ , two additional routes are possible. The first is by the water-gas shift reaction of  $\text{CO}$  and  $\text{H}_2\text{O}$  to give  $\text{H}_2$ , which then reacts with  $\text{NO}$  to give  $\text{NH}_3$ . A second pathway is through reaction between  $\text{NO}$  and  $\text{CO}$  forming support bound isocyanate ( $-\text{NCO}$ ) species, which are hydrolyzed by water to form  $\text{NH}_3$ . The contribution of both pathways is of significance because each proceeds in the presence of  $\text{H}_2\text{O}$  which is obviously in high concentration in the exhaust (5-10%) but without  $\text{H}_2$  in the feed, which is typically low in diesel exhaust. However, the major pathway leading to  $\text{NH}_3$  is still unclear and the kinetics of  $\text{NH}_3$  formation has not been properly determined. This study focuses on the  $\text{NH}_3$  formation mechanism.

#### 4. Immobilizing Catalysts on Oxide Supports by Chelate Phosphine Linkers with Long Alkyl Chains

Johannes Guenther and Janet Blüemel\*

Department of Chemistry, Texas A&M University, PO Box 30012, College Station, TX 77842, [jguenther@chem.tamu.edu](mailto:jguenther@chem.tamu.edu)

A new class of tridentate phosphine ligands with the general formula  $[\text{MeP}\{(\text{CH}_2)_x\text{PPh}_2\}_3]^+\text{I}^-$  ( $x = 4, 7, 11$ ), and  $[\text{MeP}(\text{CH}_2\text{PPh}_2)_3]^+\text{OTf}^-$ , have been synthesized and fully characterized.<sup>1</sup> The linkers have been immobilized on silica with their phosphonium moieties via electrostatic interactions, and their mobility and leaching has been studied by solid-state HRMAS (high-resolution magic angle spinning) NMR. Immobilized Wilkinson-type rhodium complexes have been obtained by ligand exchange with the surface-bound linkers.<sup>1</sup> The activities and lifetimes of the catalysts have been tested with respect to the hydrogenation of 1-dodecene. The rhodium catalyst precursor bound by the immobilized linker  $[\text{MeP}\{(\text{CH}_2)_7\text{PPh}_2\}_3]^+\text{I}^-$  led to material with the highest activity and lifetime, and it could be recycled for a record 30 times. For all catalysts the formation of rhodium nanoparticles with narrow size distributions around 4 nm has been proven.<sup>1</sup>



1. J. Guenther, J. Reibenspies, J. Blüemel, *Adv. Synth. Catal.* 2011, 353, 443-460.

#### 5. Mixed Rare-Earth Oxides (REOs) for Hot Gas Desulfurization and Tar Removal from Gasifier Effluents

Rui Li, Joseph Bridges, and Kerry Dooley

Louisiana St. Univ., Dept. of Chemical Engineering  
[ri9@tigers.lsu.edu](mailto:ri9@tigers.lsu.edu) (Rui Li)

We are studying REO/transition metal catalytic systems capable of reforming/cracking typical tar model compounds (e.g., naphthalene) at  $<750^\circ\text{C}$  in realistic biomass/coal gasifier effluents containing water,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{S}$ .  $\text{MnO}_x$  or  $\text{FeO}_x$  look like good candidates in combination with  $\text{CeO}_2/\text{La}_2\text{O}_3$ -based REOs, either unsupported or supported on high-temperature  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3/\text{ZrO}_2$ . We are examining the effects of effluent composition (especially  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ ) and temperature on the naphthalene reactions, and trying to map out the reaction pathway. We are also conducting lifetime studies, and using XANES/EXAFS to determine changes in the adsorbents/catalysts over several cycles of use.

For effluents with higher levels of sulfur, desulfurization must precede the tar reactions, and for this purpose we have shown that similar materials can act as regenerable adsorbents in the 600-650°C range.



## 6. Study on Pure-silica Zeolite Nucleation and Growth from Solution

Xiang Li and Daniel F. Shantz

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX

Zeolites are micro-porous crystalline materials, which are widely used in catalysis, adsorption, and ion-exchange processes<sup>[1]</sup>. However, in most cases, synthesis of novel zeolites still relies on trial-and-error method, which is time consuming and expensive. The purpose of this research is to understand zeolite formation mechanism, and further develop *a priori* knowledge for rational design of zeolite nanocrystals as industrial catalysts, thin film and nano-devices<sup>[2]</sup>. In this work, the formation of silicalite-1 (pure-silica ZSM-5) from aqueous solution of tetraethylorthosilicate (TEOS) and tetrapropylammonium hydroxide (TPAOH) was studied<sup>[3-5]</sup>. The Investigation focused on the evolution of silica precursor particles (2-5 nm) which are formed from TEOS hydrolysis and serve as building units in silicalite-1 synthesis. Also quantitative analysis of interactions between these silica particles and TPA cations were performed using Scattering techniques (DLS, SAXS) and Nuclear Magnetic Resonance (NMR) method. Furthermore, thermodynamics and kinetics prior to and during zeolite nucleation were studied. These research results provide important technical basis for synthesis of pure-silica zeolite in an efficient and economic approach.

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## 7. Improving Selectivity in Oxydesulfurization (ODS)

Andrew Madrid, Dongxing Liu, F. Carl Knopf and Kerry Dooley

Louisiana St. Univ., Dept. of Chemical Engineering  
[ammadrid@gmail.com](mailto:ammadrid@gmail.com) (Andrew Madrid)

In oxydesulfurization (ODS), S-heterocycles (e.g., thiophene, DBT) are oxidized, then removed by adsorption or extraction. Conditions mild relative to HDS, with temperatures usually <120°C. Oxidants which have been studied include H<sub>2</sub>O<sub>2</sub>, surface-bound -OOH, organic peroxides, aldehydes with O<sub>2</sub>, and O<sub>2</sub> itself. Refractory compounds in HDS (e.g., 4,6-dimethyldibenzothiophene) are sometimes more reactive than thiophene or DBT in ODS. The goal is to make sulfones, which are highly polar and can be extracted with (e.g.) CH<sub>3</sub>CN, DMF, NMP, DMSO, methanol or water itself.

The chief problem with ODS is the low selectivity, since alkylaromatics in diesel are also oxidized. In fact, we have shown that with O<sub>2</sub> the reaction is actually heterogeneous-homogeneous and the oxidized alkylaromatics can act as radical chain carriers to further the oxidation of the S-heterocycles. Two classes of catalysts which give higher selectivity with O<sub>2</sub> include Pd/C and Mo<sub>2</sub>C/C. Results of studies done in small semibatch reactors and in a larger microreactor system designed to eliminate the influences of diffusion on the main reactions will be presented, for a model number 2 diesel.

## 8. Role of NO and NO<sub>2</sub> on the Kinetics of the Selective Catalytic Reduction of NO<sub>x</sub> with NH<sub>3</sub> on Fe-ZSM-5

Pranit S. Metkar, Michael P. Harold and Vemuri Balakotaiah

Department of Chemical & Biomolecular Engineering, University of Houston, Houston, TX, United States.





A comprehensive experimental study of steady-state and transient selective catalytic reduction (SCR) of  $\text{NO}_x$  with  $\text{NH}_3$  on both commercial and in-house synthesized Fe-ZSM-5 (MFI type) monolith catalysts is carried out.  $\text{NO}_2$  present in the inlet feed was found to accelerate the  $\text{NO}_x$  reduction at lower temperatures during both the steady state and transient experiments with the maximum selectivity towards  $\text{N}_2$  obtained for a feed containing an equimolar ratio of  $\text{NO}/\text{NO}_2$  over a wide temperature range (150-500 °C). Presence of  $\text{NO}_2$  leads to the formation of ammonium nitrate which inhibits the  $\text{NO}_x$  conversion for both the fast and  $\text{NO}_2$  SCR reactions. The presence of  $\text{NO}$  facilitates the reduction of nitrate, perhaps in the form of  $\text{HNO}_3$ , and is shown to be a key step for the fast SCR chemistry. Unlike standard SCR,  $\text{NH}_3$  shows little inhibition of the fast SCR reaction and no inhibition of the  $\text{NO}_2$  SCR reaction. Based on these data and previous literature results, a SCR mechanism is developed and corresponding kinetic model derived. Experiments with monolith catalysts having different washcoat thicknesses indicate the presence of washcoat diffusion limitations for both the standard SCR reaction (Temperatures  $\geq 350$  °C) and fast and  $\text{NO}_2$  SCR reaction (Temperatures  $\geq 200$  °C), which underscores the need to account for this transport process in modeling studies.

## 9. Prediction of Propene Oligomerization Activity of Different Cationic Forms of Y-Zeolite Based on Infrared Molar Absorption Coefficients

Huong T. Ngo, Friederike C. Jentoft

School of Chemical, Biological and Materials Engineering, University of Oklahoma, Norman OK 73019

\*[thuong.ngo-1@ou.edu](mailto:thuong.ngo-1@ou.edu), [fcjentoft@ou.edu](mailto:fcjentoft@ou.edu).

A novel method of using IR spectra to assess the reactivity of molecules adsorbed on catalysts is proposed. By relating the band intensity of a vibration to the number of adsorbed species, the molar absorption coefficient can be calculated. This parameter depends on the change in dipole moment during bond stretching and should reflect how easily the bond can be activated for heterolytic cleavage. Our hypothesis is that higher values of molar absorption coefficients indicate stronger bond polarization by the surface, which should result in a lower activation energy and thus generally lower reaction temperatures.

In this work, we (1) demonstrate a method to measure the molar absorption coefficients of the vibrations of propene adsorbed on different cationic forms of zeolite Y ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and (2) show a correlation between the molar absorption coefficients of the C=C vibration and C=C bond reactivity. Experimental results reveal that in the order of NaY, CaY and MgY, (1) the C=C vibrations of adsorbed propene have increasing molar absorption coefficient values of 13, 16 and 21 km/mol, and (2) the oligomerization occurs at progressively decreasing temperature, which agrees with our hypothesis.

## 10. Highly Stable Ru Pyrochlores for Syngas Production

Devendra Pakhare<sup>1</sup>, Sarthak Gaur<sup>1</sup>, James J. Spivey<sup>1\*</sup>

<sup>1</sup> Cain Chemical Engineering Department, Louisiana State University, Baton Rouge, LA 70803.

Methane reforming using carbon dioxide as oxidant to produce synthesis gas ( $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ ) has received considerable attention as it involves consumption of two green-house gases to give industrially important products. Here we report the results of this reaction on two catalysts: 1% Ru metal substituted in the pyrochlore ( $\text{La}_{1.97}\text{Sr}_{0.03}\text{Ru}_{0.47}\text{Zr}_{1.53}\text{O}_7$ ) and 0.5% Ru/ $\text{Al}_2\text{O}_3$  as a baseline comparison. This is a highly endothermic reaction ( $\Delta H_{298\text{K}} = 261 \text{ kJ mol}^{-1}$ ) and requires high temperatures to attain high conversion to syngas. Pyrochlores were tested for this reaction at 600°, 700° and 800°C. The similarity of XRD data of the fresh and spent pyrochlores confirms their structural stability at these high temperatures. TPR of the two catalysts suggest that the substitution of the metal into the pyrochlore structure results in higher reduction temperature than

0.5% Ru/Al<sub>2</sub>O<sub>3</sub> indicating higher co-ordination of the surface metal of pyrochlores than the supported catalysts. Methane conversion over 0.5% Ru/Al<sub>2</sub>O<sub>3</sub> shows deactivation at 600°C whereas pyrochlores show constant conversion for the time on stream. Apparent higher CO<sub>2</sub> conversion and lower H<sub>2</sub>/CO ratio over 0.5% Ru/Al<sub>2</sub>O<sub>3</sub> compared to pyrochlores suggest the occurrence of reverse water gas shift over baseline catalysts, which is not evident over pyrochlores.

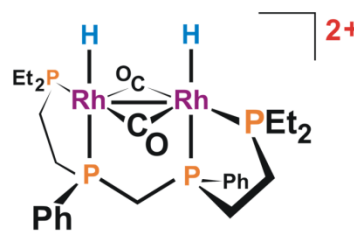
\*To whom correspondence should be addressed. Tel. (+1) 225-578-3690. E-mail: [jjspivey@lsu.edu](mailto:jjspivey@lsu.edu)

## 11. Hydroformylation by a Dirhodium Tetraphosphine Catalyst: New Revelations

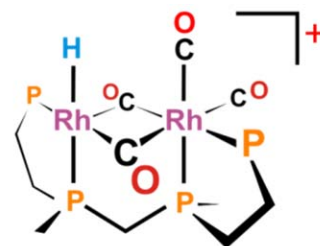
Darina Polakova, Catherine Thomas, George Stanley\*

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804

We have developed a tetraphosphine ligand capable of bridging and chelating two rhodium centers. The *racemic* form of the catalyst precursor, [Rh<sub>2</sub>(nbd)<sub>2</sub>(*rac*-et,ph-P4)](BF<sub>4</sub>)<sub>2</sub>, showed hydroformylation performance comparable to the best monometallic Rh-phosphine systems known.[1] The active catalyst based on all our spectroscopic work is proposed to be [Rh<sub>2</sub>H<sub>2</sub>(CO)<sub>2</sub>(*rac*-et,ph-P4)]<sup>2+</sup>. DFT computational studies also support this assignment. High-pressure NMR and FT-IR spectroscopy shows fairly rapid degradation of the dirhodium catalyst in acetone, but via a very different mechanism than monometallic Rh-phosphine complexes.



The dirhodium catalyst has far better hydroformylation performance when water is used as a co-solvent.[2] This work continues NMR and FT-IR studies in acetone and acetone/water to understand some of the anomalies from the previous work. Additionally, spectroscopic studies of *meso*-[Rh<sub>2</sub>(nbd)<sub>2</sub>(et,ph-P4)]<sup>2+</sup> were performed for the first time. NMR studies were performed under H<sub>2</sub>/CO pressure using d<sub>6</sub>-acetone without or with H<sub>2</sub>O. Based on our preliminary results, we propose as the main catalytic species in acetone is the originally proposed dicationic dihydride and in acetone/water monocationic monohydride species shown to the right. Both catalysts operate via very effective bimetallic cooperativity, but the details of their catalytic mechanisms, activities, and stabilities differ considerably.



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## 12. Regulation of the Hydrodechlorination Catalytic Activity of Pd-on-Au Nanoparticles Through Au Particle Size

Lori A. Pretzer<sup>1</sup>, Hyun J. Song,<sup>1</sup> Yu-Lun Fang,<sup>2</sup> Zhun Zhao,<sup>2</sup> Neng Guo,<sup>3</sup> Tianpin Wu,<sup>4</sup> Jeffrey T. Miller,<sup>4</sup> and Michael S. Wong<sup>1,2\*</sup>

Department of Chemistry, Rice University<sup>1</sup>

Department of Department of Chemical and Biomolecular Engineering, Rice University,<sup>2</sup>

Conversion Technology Center, BP Products,<sup>3</sup>

Chemical Sciences and Engineering Division, Argonne National Laboratory,<sup>4</sup>

Trichloroethene (TCE), an excellent degreasing agent, is a common and carcinogenic toxin currently present in the groundwater of several industrialized nations. Conventional TCE remediation techniques are time-consuming, expensive, and merely sequester the contaminant in a different environment sector so that it remains a potential threat. Recently we discovered that 4 nm Au nanoparticles (NPs) with submonolayer surface coverages of Pd (Pd-Au NPs) could quickly and selectively hydrodechlorinate TCE to ethane at room temperature. We further probed the activity of our Pd-Au NPs by varying the size of the Au core between ~3 nm and ~10 nm. We found that Pd-Au NPs with 7 nm Au cores exhibit higher activity (~3,500 L/g<sub>Pd</sub>/min) than our previous 4 nm Pd-Au NPs (> 1,900 L/g<sub>Pd</sub>/min) and conventional Pd/Al<sub>2</sub>O<sub>3</sub> (29 L/g<sub>Pd</sub>/min). While the selectivity of the catalysts is the same, their activity changes with the Au particle size and Pd surface coverage (Pd SC). Using x-ray absorbance spectroscopy (XAS), we discuss how the aggregation state of the Pd atoms, which changes with Pd SC and Au particle size, affects the NP's catalytic activity.

### 13. In-situ PFG NMR Investigations of Silicalite-1 Synthesis

Alejandra Rivas-Cardona and Daniel F. Shantz\*

Artie McFerrin Department of Chemical Engineering  
Texas A&M University, College Station, Texas 77843-3122

In-situ pulsed field gradient nuclear magnetic resonance (PFG NMR) spectroscopy was used to study the organocation-silica interactions in the silicalite-1 synthesis at 70°C from mixtures of tetrapropylammonium hydroxide (TPAOH), tetraethyl orthosilicate (TEOS) and water. PFG NMR results show that the diffusion coefficients of the TPA cation at 70°C follow similar trends than those observed in mixtures at 25°C. However, the adsorption isotherms at 70°C do not fit to a Langmuir isotherm as well as they do at 25°C. Therefore, the Freundlich isotherm was used to fit the adsorption data from which adsorption Gibbs energies between 6 and 15 kJ/mol were obtained. Time evolution studies were also performed on a TPAOH-TEOS-water mixture. These studies show that the TPA diffusion coefficients remain almost constant at the beginning of the synthesis, start to increase with the onset of turbidity, reach a maximum at about 6 days, and trend to a plateau towards the end of the synthesis. The maximum in the diffusion coefficient of the TPA cation is associated with the exothermic-endothermic transition that is known to occur near to the completion of the synthesis. The results of this work show that organocation-silica interactions can be studied at the synthesis conditions by monitoring the diffusion coefficients of the organocation with in-situ PFG NMR. Thus, changes in the diffusion coefficients of the organocation might be associated with conformational changes of the silica species.

### 14. A Comparative Study of Pd Catalysts and Fe Reductants for Water-phase Trichloroethene Hydrodechlorination

Shujing Li,<sup>†,‡</sup> Yulun Fang,<sup>‡</sup> Chris D. Romanczuk,<sup>‡</sup> Zhaohui Jin,<sup>†</sup> Tielong Li,<sup>†</sup> Michael S. Wong<sup>\*,‡,§,||</sup>

<sup>†</sup> College of Environmental Science and Engineering, Nankai University, 94 Weijin Road, Tianjin, 300071, P. R. China

<sup>‡</sup> Department of Chemical and Biomolecular Engineering, Rice University, 6100 Main Street, Houston, TX 77005, USA

<sup>§</sup> Department of Chemistry, Rice University, 6100 Main Street, Houston, TX 77005, USA

<sup>||</sup> Center of Biological and Environmental Nanotechnology, Rice University, 6100 Main Street, Houston, TX 77005, USA

\* Corresponding author phone: +1 713 348 3511 fax: +1 713 348 5478 E-mail: [mswong@rice.edu](mailto:mswong@rice.edu)

Groundwater treatment through Pd-based *ex-situ* catalytic or Fe-based *in-situ* reductive breakdown of undesired contaminants has many advantages over the current physical displacement methods. Here, the reaction rates, chemical pathways, and breakdown products of these two chemical methods are compared for the first time. Through room-temperature, constant-pH, batch-reactor studies of trichloroethene hydrodechlorination, pseudo-first order reaction rate constants were determined to be 11900±1200, 1000±200, 450±30, 2.41×10<sup>-4</sup>,

$4.2 \times 10^{-4}$ , and  $7.09 \times 10^{-6}$  L/g-metal/min for Pd-on-Au Nanoparticles (Pd/Au NPs), Pd NPs, Pd-on-Alumina (Pd/Al<sub>2</sub>O<sub>3</sub>) powder, NANOIRON 25S, NANOIRON 25 and Hepure H-200, respectively. Pd-based materials were at least 6 orders of magnitude more active than Fe-based materials. The major products were ethene and ethane with all materials, and carbon mass balances of ~90% were achieved with all except H-200 iron powder. Ethene as a transient intermediate disappeared soon for Pd catalyzed TCE dechlorination, while for nanoscale iron particles, the transformation from ethene to ethane was relatively slow. Ethene began to be converted into ethane when more than 90% of TCE was reduced. pH can affect reaction rate through deactivating Pd catalyst in different degrees with different pH on Pd/Au NPs catalytic TCE dechlorination. When pH was below 5.50,  $k_{cat}$  dropped dramatically with pH decreasing.

## 15. Alkene Oxidative Cleavage by O<sub>2</sub> and Bimetallic Nickel Phosphine Complexes

Bill Schreiter, Katerina Kalachnikova, Ciera Duronslet, & George Stanley\*

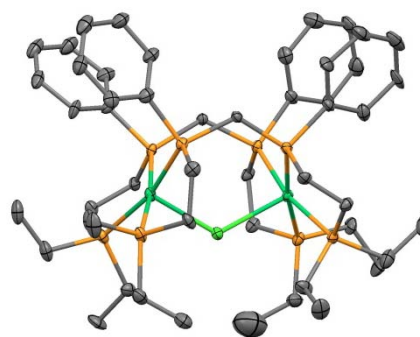
Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804

Bimetallic *meso*-Ni<sub>2</sub>X<sub>4</sub>(*et,ph*-P4) complexes (X = Cl, Br), (*et,ph*-P4 = Et<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)(Ph)PCH<sub>2</sub>P(Ph)-(CH<sub>2</sub>CH<sub>2</sub>PEt<sub>2</sub>) in the presence of oxygen and in water/polar organic solvent solutions show activity as precursors for the oxidative cleavage of unactivated alkenes to cleanly produce aldehyde products as shown below.

Alkenes tested include: 1-hexene, 1-octene, cyclohexene, cyclopentene, and styrene, trans-stilbene, trans-5-decene. Aldehyde and dialdehyde products have been characterized by gas chromatography-mass spectrometry (GC/MS) and NMR spectroscopy. No phosphine ligand oxidation has been observed except under very forcing conditions.

Although the current system is not currently catalytic spectroscopic studies indicate that the reason for this is transformation of the active dinickel complex into an inactive species, [Ni<sub>2</sub>(μ-Cl)(*meso-et,ph*-P4)<sub>2</sub>]<sup>3+</sup>, which has been characterized by X-ray crystallography and shown to the right.

Although monometallic NiCl<sub>2</sub>(*dppe*) and NiCl<sub>2</sub>(*dcpe*) complexes are also active for oxidative cleavage of alkenes using O<sub>2</sub> and H<sub>2</sub>O/polar organic solvent, they do not make as much aldehyde as bimetallic complex nor as quickly. NiCl<sub>2</sub>(*dppp*) and NiCl<sub>2</sub>(*tpp*)<sub>2</sub> were not active under conditions tested. Reactions with





norbornene and norbornadiene do not yield any products. Possible reaction mechanisms have been proposed based on DFT computational studies and will be presented.

## 16. Solvothermal Synthesis of Ultrasmall, Metathesis-active Tungsten Oxide Nanoparticles

Nik Soultanidis<sup>a</sup>, Wu Zhou<sup>b</sup>, Christopher J. Kiely<sup>b</sup>, and Michael S. Wong<sup>a,c</sup>

<sup>a</sup>Dept. Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, USA

<sup>b</sup>Dept. of Materials Science & Engineering, Lehigh University, Bethlehem, PA 18015, USA

<sup>c</sup>Dept. of Chemistry, Rice University, Houston, TX 77005, USA

The synthesis of metal oxide ( $\text{MO}_x$ ) nanoparticles (NPs) of metals such as tungsten, molybdenum and vanadium is of great significance in materials chemistry with applications in catalysis, semiconductors, gas sensors and optoelectronics. Recent discoveries in the field of catalysis have highlighted the need for the controlled synthesis of ultra-small ( $< 2$  nm) tungsten oxide ( $\text{WO}_x$ ) NPs that has not been achieved by conventional methods.

In this work, we introduce a solvothermal synthesis route to ultra-small  $\text{WO}_x$  NPs using ammonium polyanionic salts and oleylamine stabilizing ligand. Consistently producible in high yields ( $92 \pm 5\%$ ), the resultant oleylamine-coated  $\text{WO}_x$  NPs were partially crystalline with a core of 20-36  $\text{WO}_x$  structural units as determined from aberration-corrected high-resolution scanning transmission electron microscopy and a shell of 16-20 oleylamine molecules as determined by thermogravimetric analysis. The NPs had a mean size of 1.6 nm and a relative standard deviation (RSD) of 16%, as estimated from atomic force microscopy.

$\text{WO}_x$  NPs were immobilized onto a  $\text{SiO}_2$  support and calcined. The oleylamine suppressed  $\text{WO}_x$  NP sintering during calcination, allowing for higher loadings of  $\text{WO}_x$  species than typically possible. Evaluated for the gas-phase reaction of propylene metathesis, this material was found to be up to 2 times more selective for ethylene/butylene metathesis products than conventionally prepared  $\text{WO}_x/\text{SiO}_2$ . The selectivity enhancement may be due to more desirable active sites provided by the smaller  $\text{WO}_x$  domains in combination with residual oleylamine on the catalyst.

## 17. Cobalt Particle Size Effect in Fischer-Tropsch Synthesis

Stephanie Skiles, Zhou-jun Wang, Fan Yang, Zhen Yan, and D. Wayne Goodman

Department of Chemistry, Texas A&M University, College Station, TX 77843, United States

Cobalt and iron are commercially used metal catalysts for Fischer-Tropsch Synthesis. Although it is more expensive, cobalt is preferred due to its higher activity, higher chain growth probability, and lower water-gas shift activity. Due to its expense, an optimal design of the catalyst is essential. The effect of cobalt particle size was studied on  $\text{Co}/\text{SiO}_2$  model catalysts that were prepared and characterized in an ultrahigh vacuum chamber. The catalyst were prepared with various metal coverages ranging from 0.25 -6.0 monolayers, corresponding to particle sizes from 1.4 – 10.5 nm, as determined by TEM analysis. The FT reaction was carried out at atmospheric pressure in a batch reactor at 513K. Small cobalt particles (1.4 – 2.5 nm) showed a lower TOF and higher  $\text{CH}_4$  selectivity. This was attributed to the cobalt surface being readily oxidized by the water vapor produced during the reaction. This oxidation was confirmed by post-reaction XPS analysis. Larger cobalt particles did not show oxidation, resulting in relatively constant reactivity and selectivity. The lack of particle size effect for the larger particles is consistent with the reported structure insensitivity for FT synthesis.

## 18. Synthesis and Characterization of Sn(IV) MFI: Sodium Inhibits the Synthesis of Phase Pure Materials



Nataly Garcia Vargas, Scott Stevenson and Daniel F. Shantz\*

Artie McFerrin Department of Chemical Engineering  
Texas A&M University

3122 TAMU, College Station, TX 77843-3122,

Phone: (979) 845-3492, Fax: (979) 845-6446.

\* Correspondence: Daniel F. Shantz. [shantz@chemail.tamu.edu](mailto:shantz@chemail.tamu.edu)

The catalytic properties of zeolites are directly related to the presence of heteroatoms in their crystalline framework. For aluminum-containing zeolites, the charge deficiency created by the presence of aluminum in the framework confers the zeolites with acid centers that can be modulated to target a wide range of applications in solid acid catalysis. The titanium-substituted Ti-Si-1 zeolite has proven to be active in several industrially important redox reactions in which the ability of titanium to change its coordination is exploited. Tin-containing zeolites are interesting because they can potentially be active in Lewis acid catalyzed reactions. Sn-Beta is a tin substituted zeolite made in fluoride media that catalyzes reactions such as the Baeyer-Villiger oxidation and the MPV reduction of cyclic and linear ketones with remarkable selectivities. The synthesis of Sn-MFI in hydroxide media has also been reported and different synthesis pathways have been explored to obtain high substitution. However, a more detailed description about how pH and presence of alkali cations such as sodium affect the synthesis is lacking. In this work, the synthesis of Sn-MFI in hydroxide media is reported. By using several characterization techniques such as PXRD, XRF, XPS, SEM, UV-Vis among others, it will be shown that sodium ions lead to the formation of impurities that have a detrimental effect on the properties of the materials but also it will be shown that by manipulating the pH of the gels one can have a control of the impurities and phase pure materials can be obtained. Additionally to that, the activity of these materials on the hydroxylation of phenol reaction will be also presented.

## 19. The Effect of Adsorbed Water in CO Oxidation on Au/TiO<sub>2</sub>(110)

Ting Yan, Jinlong Gong, David W. Flaherty, and C. Buddie Mullins

The effect of moisture on CO oxidation on Au/TiO<sub>2</sub>(110) model catalysts is investigated using temperature-programmed desorption and molecular beam reactive scattering under ultrahigh vacuum (UHV) conditions. Oxygen exchange is observed between adsorbed atomic oxygen and isotopically labeled water. Coadsorbed water (H<sub>2</sub><sup>18</sup>O) takes part in CO oxidation on O<sub>a</sub> precovered Au/TiO<sub>2</sub>(110) model catalysts, leading to the formation of C<sub>16</sub>O<sub>18</sub>O and C<sub>16</sub>O<sub>16</sub>O. The amount of C<sub>16</sub>O<sub>18</sub>O produced increases with increasing water coverages; however, the total amount of CO<sub>2</sub> produced decreases. Although coadsorbed O<sub>a</sub> and H<sub>2</sub>O have a minimal influence on the initial adsorption probability of CO, the total uptake of CO decreases as H<sub>2</sub>O coverages increase. Interestingly, the adsorption of water induces desorption of predeposited molecularly chemisorbed O<sub>2</sub>. Thus, adsorbed water slightly inhibits CO oxidation on atomic oxygen precovered Au/TiO<sub>2</sub>(110) model catalysts under UHV conditions.

## 20. Preparation and Characterization of Ni-Au Bimetallic Model Catalysts

Fan Yang, Yunxi Yao, Zhen Yan, Hlaing Min Li Liu and D. Wayne Goodman\*

Department of Chemistry, Texas A&M University, College Station, TX 77843

Nickel-gold bimetallic catalysts have been shown interesting catalytic properties for a variety of reactions, such as steaming reforming of hydrocarbons, hydrodechlorination and selective hydrogenation of alkynes. In this study, we employed low energy ion scattering spectroscopy (LEIS) and polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) to study the Ni-Au alloy surface composition and related gas adsorption. Ni-Au bimetallic model catalysts were prepared as thin films on Re(0001) and Ru(0001) substrates by physical vapor



deposition under ultrahigh vacuum conditions. The surface compositions and electronic structures of the Ni-Au model catalysts were characterized by LEIS and X-ray photoelectron spectroscopy (XPS). Ni-Au thin films form a stable surface alloy between 500 and 800 K with substantial enrichment of Au compared to the bulk compositions. Annealing a Ni-Au thin film with a 1:1 composition ratio at 600 K results in a surface alloy with 84% (atomic concentration) of Au in the outermost surface layer. Molecular CO, which only absorbs on Ni sites at room temperature, was used as a probe to study the surface atomic structure. At saturated coverage, CO adsorption IR spectra show decrease or disappear of two-fold bridge site CO adsorption on Ni atoms with the increase of Au surface atomic concentrations. The absence of Ni bridge site CO adsorption indicates that Ni atoms are mostly isolated by Au atoms on annealed Ni-Au alloyed surfaces.

## 21. Energetic Nanoparticles as Fuel Additives for Enhanced Performance in Propulsion Systems

Neng Wang, Jacob Hanberry, Srinibas Karmakar, Sumanta Acharya and Kerry Dooley

Louisiana St. Univ., Dept. of Chemical Engineering  
[nwang5@lsu.edu](mailto:nwang5@lsu.edu) (Neng Wang)

The goal of this project is to combine energetic boron nanoparticles, which can be used to enhance emission and heat release in liquid combustion systems, with more conventional oxidation catalysts, as core-shell nanoparticles. The boron nanoparticles themselves can be ignited by other catalytic agents, such as rare earth oxides, or suboxides of the group V-VIII transition metals. The oxidation catalysts can fulfill a second function, in that they can protect the energetic nanoparticles from oxidation during storage and handling, if present as a shell. Various syntheses of such materials are being explored.

Based on limited data, it appears that these core-shell nanoparticles are superior to conventional boron nanoparticles in the combustion of ethanol. The temperature of the system at the burner (the dump plane) increases, and combustion is more complete at a constant equivalence ratio. Combustion data and some before and after structural characterizations of the nanoparticle composites will be presented.

## 22. Planar Oxide Supported Platinum Nanoparticles as Model Catalysts

Xin Wang, Matthew Lundwall, Sean M. McClure, Zhoujun Wang, D. Wayne Goodman

Department of Chemistry, Texas A & M University, College Station, Texas, USA

The surface-science approach to heterogeneous catalysis is the employment of well-defined surfaces to reaction systems. In this regard, the study of reactions on metallic single-crystals have provided a wealth of information and have set the foundation for advanced study of heterogeneous catalysts as they provide a reference for complex systems. These surfaces have helped elucidate the relation between surface-structure and its influence on reactivity and selectivity. Advanced work on model-surfaces continues to approach the complexity seen on technical catalyst surfaces by the analysis of oxide-support surfaces in ultra-high vacuum (UHV), e. g. Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> surfaces which are prevalent in industrial-scale catalysis.

Here, we create Pt/SiO<sub>2</sub> model catalysts in UHV and characterize the surface using Auger electron spectroscopy (AES), temperature programmed desorption (TPD), infrared reflection absorption spectroscopy (IRAS), and elevated-pressure (>8torr) reactivity measurements. Results demonstrate the utility of well characterized model catalyst samples in obtaining qualitative and quantitative reactivity data at elevated pressures. These surfaces allow study of support- and particle-size- effects while being amenable to surface spectroscopies. The insights gained from oxide-supported model systems bridges the material gap between single crystal and



technical catalysts, and establishes a second tier in the surface approach to heterogeneous catalysis.

### 23. Exploration of Intrinsic Activity of Platinum for Water-Gas Shift Reaction

Wen-Yueh Yu,<sup>1</sup> David W. Flaherty,<sup>1</sup> Zachary D. Pozun,<sup>2</sup> Graeme Henkelman<sup>2</sup>, C. Buddie Mullins<sup>1,2\*</sup>

<sup>1</sup> Department of Chemical Engineering, <sup>2</sup> Department of Chemistry and Biochemistry, Center for Electrochemistry, Texas Materials Institute, and Center for Nano- and Molecular Science, University of Texas at Austin, 1 University Station C0400, Austin, Texas 78712

\* [mullins@che.utexas.edu](mailto:mullins@che.utexas.edu)

The catalytic activity of monofunctional Pt (*i.e.*, without a support) for the water-gas shift reaction (WGSR) is investigated using a Pt(111) single crystal at relevant conditions. Pt(111) catalyzes WGSR with an activation energy of 96 kJ mol<sup>-1</sup>, a value greater than those found on oxide supported Pt clusters. The turnover frequency (TOF) increases sublinearly with P<sub>H<sub>2</sub>O</sub>, consistent with a low coverage of activated H<sub>2</sub>O under all conditions. Negative TOF dependence on P<sub>CO</sub> at low temperature confirms that the surface is largely covered by CO which can inhibit H<sub>2</sub>O activation; at higher temperature the TOF rises linearly and then plateaus with increasing pressure demonstrating the transition from a predominantly empty surface to a CO saturated surface. Using deuterated water, a normal kinetic isotope effect was observed illustrating the kinetic relevance of O-H/D bond rupture. Under the same conditions (10 Torr H<sub>2</sub>O and 26 Torr CO at 612 K) the TOF of Pt(111) is 0.53 ± 0.03 H<sub>2</sub> site<sup>-1</sup>sec<sup>-1</sup>, ~ 5 times greater than that of Cu(111). The activity decays with time, a process which by the nature of this system *cannot* be due to sintering or agglomeration, and is attributed to carbon deposition based on AES observation and DFT calculations.

### 24. Enhanced Efficiency of Perchloroethene Removal and Selective Oxidation of Glycerol Using Pd-on-Au Bimetallic Catalysts

Zhun Zhao<sup>1</sup>, Yu-Lun Fang<sup>1</sup>, Joni Arentz<sup>5</sup>, Pedro J.J. Alvarez<sup>3, 4</sup>, and Michael S. Wong<sup>1, 2, 4</sup>

<sup>1</sup>Department of Chemical and Biomolecular Engineering, [zz6@rice.edu](mailto:zz6@rice.edu)

<sup>2</sup>Department of Chemistry,

<sup>3</sup>Department of Civil and Environmental Engineering,

<sup>4</sup>Center for Biological and Environmental Nanotechnology, Rice University, 6100 South Main Street, Houston, TX, 77005,

<sup>5</sup>Department of Chemical and Biomolecular Engineering, University of Groningen, The Netherlands

PCE (perchloroethene) is a common environmental contaminant in groundwater and one of dense non-aqueous phase liquids (DNAPLs). Hydrodechlorination (HDC) using palladium based catalysts is an efficient way to remove PCE. Glycerol is a byproduct from biodiesel production in very large quantity, and the green conversion of it into more valuable products is being studied over the years using noble metals. Palladium-on-gold (Pd/Au) bimetallic catalysts prepared from tannic acid-sodium citrate and hydrogen reduction method have shown their enhanced high activity for both HDC of PCE and selective oxidation of glycerol. In HDC reaction, the Pd/Au NPs had much higher catalytic activities (pseudo-first order rate constant was 4682 L/g<sub>Pd</sub>/min at 80% Pd surface coverage) over other Pd catalyst materials such as Pd/Alumina and Pd NPs; which had the rate constants of 60.4 and 238 L/g<sub>Pd</sub>/min, respectively. The catalysts activity shows a volcano shape pattern when plotted against the Pd surface coverage, with the most active one at ~80% coverage. In selective oxidation of glycerol reaction, 80% Pd/Au supported on active carbon catalyst was four times more active than pure Au and pure Pd catalysts under the experimental condition, and the selectivity towards glyceric acid was found to be enhanced to 75% at 40% conversion. The synergistic effect of Pd and Au plays a big role in the enhancement





in both reactions. Pd/Au bimetallic catalysts offer a promising way to remove PCE from contaminated groundwater and to convert glycerol into more valuable compounds.

## **25. The 2-D Growth of Gold on Single-layer Graphene/Ru(0001): Enhancement of CO Adsorption**

Zihao Zhou, Li Liu, Qinlin Guo, Zhen Yan, Yunxi Yao, and D. Wayne Goodman

The growth and morphology of two-dimensional (2-D) gold islands on a single-layer graphene supported on Ru(0001) have been studied by scanning tunneling microscopy (STM). Our findings show that gold exhibits 2-D structures up to a gold dosage of 0.75 equivalent monolayers, and that these 2-D gold islands are thermally stable at room temperature. Parallel polarization modulation infrared reflection absorption spectroscopic (PM-IRAS) and high resolution electron energy loss spectroscopic (HREELS) studies indicate that carbon monoxide (CO) adsorbs on these 2-D gold islands at 85 K, showing a characteristic CO stretching feature at  $2095\text{ cm}^{-1}$  for a saturation coverage of CO. The red shift of the CO stretching frequency compared to that on charge neutral gold is consistent with electron transfer from graphene to gold, i.e., an electron-rich gold overlayer. Preliminary data obtained by dosing molecular oxygen onto this CO pre-covered surface suggest that the 2-D gold islands catalyze the oxidation of CO.