

# SOUTHWEST CATALYSIS SOCIETY (SWCS)

## 2005 SPRING SYMPOSIUM

February 25, 2005

Farnsworth Pavilion  
Rice University  
Houston, TX

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## SOUTHWEST CATALYSIS SOCIETY

**To: Members of the Southwest Catalysis Society (SWCS)**

From: Yun-feng Chang, Chair-Elect

The 2005 SWCS Spring Symposium will be held on Friday Feb. 25, 2005, at Rice University, Houston, TX.

**Rice University** is roughly 25 miles from George Bush Intercontinental Airport and 18 miles from Hobby Airport. The symposium is to be held at the **Farnsworth Pavilion** located in the Ley Student Center/Rice Memorial/Chapel building. Detailed driving directions and maps can be obtained from <http://www.rice.edu/maps/>. (red = linked to web page)

Registration will begin at 7:45 AM and the lectures will begin at 8:05 AM. A list of podium speakers and poster presentation is given below. The 2005 Spring Symposium registration fee is \$40, which includes membership dues. For those who cannot attend the Symposium please mail in their membership due (\$25) to our Treasurer, George Stanley. A portion of the membership due goes to pay your dues to the North American Catalysis Society. Students pay \$15 (membership due included).

An update on organizing and hosting the 2007 North American Catalysis Society Meeting in Houston will be provided by Kerry Dooley. We need to update the list of members who will be interested and willing to devote time to help organize this big event. Please, let us or the other officers know if you are interested in helping to organize the event. Also, it is not too early to begin thinking about future Symposia. Please contact the SWCS officers about your interest in giving a presentation or to nominate a speaker.

I look forward to seeing you at this and future meetings.

Sincerely,

Yun-feng Chang  
Chair-Elect, SWCS

## **PROGRAM**

- 7:45-8:15 AM Registration**  
Farnsworth Pavilion, Rice University, Houston, TX
- 8:00 AM Dr. Yun-feng Chang, ExxonMobil Chemical**  
Welcoming Remarks – Chairman
- 8:05 AM Dr. Larry Murrell, Lehigh University, Lehigh, PA**  
“Advantages of Mixed Acetone-Water Sol Slurries for Coating High Temperature Stable  
Craneglas 500 Quartz Fiber Papers”
- 8:35 AM Dr. John Novak, Altalis AC Inc., Port Arthur, LA**  
“Promoting Stability of Gamma Alumina Supports”
- 9:05 AM Professor Levi Thompson, U. of Michigan, Ann Arbor, MI**  
“Catalytic and Surface Properties of Carbides and Nitrides”
- 9:35 AM Dr. Ed Sughrue, ConocoPhillips, Bartsville, OK**  
“Chemistry-Aided Design of Future Clean Fuels”
- 10:05 AM Coffee Break (Micromeritics Inc., GA)**
- 10:15 AM Professor Wayne Goodman, Texas A&M University, College Station, TX**  
“Structure-Function Relationships in Catalysis by Metal Alloys: From Single Crystals to  
Nanoparticles”
- 10:45 AM Dr. Frank Daly, Velocys Inc., OH**  
“High Efficiency Reactor for Methanol Production”
- 11:15AM Professor Michael Wong, Rice University, Houston, TX**  
“Developing Metal and Metal Oxide Nanoparticles for Heterogeneous Catalysis”
- 11:45 AM Lunch Break**
- 1:00 PM Dr. Shahid Shaikh, SABIC USA, Sugar Land, TX**  
“Oxidative Dehydrogenation of Propane over FeVAl Oxides”
- 1:30 PM Professor Daniel Resasco, University of Oklahoma, Norman, OK**  
“Combined Deep Hydrogenation and Ring-Opening of Poly-aromatic Hydrocarbons for  
Diesel Quality Improvement”
- 2:00 PM Dr. Christian Mehnert, ExxonMobil Chemical, Baytown, TX**  
“Ionic Liquid Research in the Petrochemical Industry”
- 2:30 PM Henrik W. Rasmussen and Valdis N. Berzins, Haldor Topsoe Inc., Houston, TX**  
“Production of Clean Fuel”
- 3:00 PM Poster Session (supported by ChevronPhillips Chemical; ConocoPhillips Company)**

1. **Kenneth J. Balkus Jr.\*, Minedys Macias, Thomas J. Pisklak, Decio Coutinho, Yen Yoon and Christine Proctor, UT Dallas, Richardson, TX**  
“Novel Supports for immobilization of MP-11”
2. **Leandro Balzano, Federico Scodelaro and Daniel Resasco, U. of Oklahoma, Norman, OK**  
“Single-Walled Carbon Nanotubes for Fuel Cells”
3. **Bobby Barker, Brandy Courtney and George Stanley, LSU, Baton Rouge, LA**  
“The Hydrogen Effect on a Di-nuclear Rhodium Hydroformylation Catalyst: Mechanistic Implications”
4. **Alan Bussard, F. Carl Knopf and Kerry M. Dooley, LSU, Baton Rouge, LA**  
“Hydrogenation Reactions in Catalyst Monoliths”
5. **M. S. Chen, W. T. Wallace, D. Kumar, K. Luo, Y. Cai, C. W. Yi, Z. Yan, K. K. Gath, and D. W. Goodman, Texas A&M U, College Station, TX**  
“The Structure of Catalytically Active Gold on Titania”
6. **Karen S. Kabin and Michael P. Harold, U. of Houston, Houston, TX**  
“NO<sub>x</sub> Storage and Reduction Studies on Pt/Ba/Alumina Monolithic Catalysts”
7. **D. Kumar, Y.-F. Han, M. S. Chen, Z. Yan, P. Boopalachandran and D. W. Goodman, Texas A&M U., College Station, TX**  
“Synthesis Of Vinyl Acetate Over Pd Catalysts”
8. **K. Luo, C.-W. Yi, T. Wei, and D. W. Goodman, , Texas A&M U., College Station, TX**  
“Pd-Au Model Catalysts: From Planar Surfaces to Nano-clusters”
9. **K. S. Martirosyan and D. Luss, U. of Houston, Houston, TX**  
“Novel Combustion Synthesis and Structural Characterization of Nano-Perovskites Powders”
10. **Alexandre R. Monteil, Bobby Barker, David A. Aubry, Novella Bridges, and George G. Stanley, LSU, Baton Rouge, LA**  
“Hydrocarboxylation of 1-Alkenes via a Tandem Catalysis Reaction using a Tetraphosphine Di-rhodium Catalyst System”
11. **Craig P. Plaisance and Kerry M. Dooley, LSU, Baton Rouge, LA**  
“Zeolite and Metal Oxide Catalysts for the Production of Dimethyl Sulfide and Methanethiol”
12. **Craig P. Plaisance, Arvind K. Bhat, Amitava Roy, and Kerry M. Dooley, LSU, Baton Rouge, LA**  
“X-Ray Absorption Spectroscopy of Catalysts for Methylketone Manufacture”
13. **Roberto C. Santana\*, Siriporn Jongpatiwut\*, Walter E. Alvarez\*\*, Ed L. Sughrue\*\* and Daniel E. Resasco\*, U. of Oklahoma, Norman, OK & ConocoPhillips Co., Bartsville, OK**  
“Gas Phase Kinetic Studies of Tetralin Hydrogenation on Pt/Alumina”
14. **Manish Sharma, Michael P. Harold, and Vemuri Balakotaiah, U. of Houston, Houston, TX**

“Analysis and Modeling of NO<sub>x</sub> Storage & Reduction in a Monolithic Reactor”

15. **W. T. Wallace, B. K. Min, K. K. Gath, and D. W. Goodman, Texas A&M U, College Station, TX**  
“Design of a Sinter-Resistant, Mixed-Oxide Support for Gold Clusters”
16. **Zakiya Wilson and George Stanley, LSU, Baton Rouge, LA**  
“Density Functional Investigation of a Rhodium-Catalyzed Aldehyde-Water Shift Reaction”
17. **Zakiya Wilson and George Stanley, LSU, Baton Rouge, LA**  
“The Electronic Structural Analysis of Dinuclear Rhodium Catalysts for Hydroformylation”
18. **William V. Knowles and Michael S. Wong, Rice University, Houston, TX**  
“Nanoparticle-supported Metal Oxides: WO<sub>x</sub>/ZrO<sub>2</sub> Acid Catalysts”
19. **Michael O. Nutt and Michael S. Wong, Rice University, Houston, TX**  
“Designing Pd-on-Au Nanoparticle Catalysts for Aqueous-phase Trichloroethylene Hydrodechlorination”
20. **Decio Coutinho, Zhiwei Yang, John P. Ferraris, D.J. Yang, Kenneth J. Balkus Jr., University of Texas-Dallas, Richardson, TX**  
“Mesoporous Carbon Molecular Sieves from Mesoporous Benzene Silica as Catalyst Support for Fuel Cell”

**4:30 PM Recognition for Best Poster Awards**

**4:35 PM Professor Kerry Dooley**  
Update on hosting 20th NAM 2007

**4:40 PM Business Meeting & Adjourn**

## Advantages of Mixed Acetone-Water Sol Slurries for Coating High Temperature Stable Craneglas 500 Quartz Fiber Papers

*Larry Murrell\**, *Israel Wachs*, *Elizabeth Ross*

Operando Mole.Spectroscopy & Catalysis Lab, Dept. of Chem. Eng., Lehigh University,  
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A novel concept has emerged in different laboratories that have often been referred to as a “frozen fluidized bed” of catalyst particles supported on a metal, a polymer, a fiber glass, or a quartz-like fiber paper [1, 2]. The fibers are often of ca. 10 micron diameter in an essentially random three-dimensional array where the catalyst particles are supported on the fibers may be anywhere from 0.1-20 micron in diameter. The thin paper sheets lend themselves to being formed into straight channel monolith structures, or into structured packing designs of alternating corrugated sheets [1, 2]. In the current work the advantages of mixed acetone-water sol slurries has been investigated to coat Craneglas 500 quartz-like fiber papers made from fibers that are stable at 1000<sup>o</sup>C. One of the major issues with sols, mixtures of sols, or milled catalyst slurries coated onto these fiber papers is the migration of the inorganic slurry contents following the drying front to the faces and the edges of the sample sheet. This mal-distribution of catalyst or support particles causes a catastrophic failure of the coated sheets as the fiber intersections are not attached by the coating deposit at the fiber intersections after the calcination step. So, one of the essential ingredients to making a mechanically strong final fiber papers that contain the inorganic exclusively as small particles is to have these particles serve as the “glue” of the fiber intersections. Ideal coating are obtained on these paper materials using silica, ceria, and silica-ceria mixed sols when the slurry contains ca. a 1:0.5 weight ratio of water-to-acetone. Serious mal-distribution was observed for ambient, or 120<sup>o</sup>C dried coating of these colloidal sols, or their mixture, in a water slurry. The drying of a mixed Si-Ce sol in an acetone-water slurry was followed *in situ* within the fiber network with a stereo optical microscope, and the details of the drying process was highly informative as to the different forms of the inorganic particles formed within the fiber network. This drying step proved that one of the major components of the drying process is the formation of small 3-5 micron size bubbles that begin to coalesce together to form a cluster of bubbles. As the bubbles begin to disappear the inorganic particles begin to appear as irregular shaped roughly spherical deposits, as expected. However, as the bubble cluster disappeared in certain locations it was possible to observe the unambiguous formation of thin “window-pane”, or “duck’s feet” structures with fibers forming the window edges. Therefore, water-acetone sol slurries have been found to solve a major coating limitation of high temperature stable quartz fiber paper sheets. In addition, acetone-water mixed sol slurries has proven of value in making gels of sol mixtures that are otherwise incompatible in aqueous solution [3]. These mixed solvent sol-gel results will be covered in this presentation, also.

### References

1. Van Der Puil, N; Carlborg, J.; Overbeek, R. A.; Chang, Y- F.; Murrell, L. L., Process for the coating metal fibrous material. PCT Int. Appl. (2001)
2. Carlborg, J A.; Chang, Y-F; Murrell, L. L.; Trubac, R. E.; Overbeek, R.A.; Schmidt, V. R.; Yeh, C. Y.; Schuh, L. Conversion of nitrogen oxides in the presence of a catalyst supported on a mesh-like structure. PCT Int. Appl. (2001)
3. Murrell, L.L., Catal. Today 35 (1997) 225-245

## Promoting the Stability of Gamma Alumina Supports

*John W. Novak, Jr., and Gerald Rzczkowski*

Almatis AC, Inc., Port Allen Works

3502 S. Riverview Drive, Port Allen, LA70767

This presentation focuses on an important industrial materials problem. Gamma ( $\gamma$ ) alumina is one of many polytypes of  $\text{Al}_2\text{O}_3$  that is used extensively as a catalyst and catalyst support (i.e., a substrate on which catalyst metal particles are dispersed). What is most often desired is the porous high surface area form of  $\gamma$ -alumina. However, at temperatures in the range 1000-1200°C,  $\gamma$ -alumina transforms rapidly into the more stable  $\alpha$ -alumina phase (1) - the pores close and catalytic activity stops. This problem is averted by promoting  $\gamma$ -alumina with one of many elements such as La or Si. Lanthanum is an expensive chemical but it can easily be incorporated with an industrial process. Other less expensive chemicals are also effective, but can be incorporated only with more expensive processes. Our scientists have demonstrated in laboratory experiments that as little as 0.3-0.5 % La can induce adequate stabilization of  $\gamma$ -alumina (2), but the industrial process generally requires 3 - 5%.

An array of complementary experimental and theoretical tools were chosen to examine the pathways of the transformation of  $\gamma$  to  $\alpha$  alumina and the role of promoters such as La and Si in impeding this process. A broad range of issues was addressed in the process of this study.  $\gamma$ -alumina has a "defect spinel" structure, namely a spinel structure in which roughly 10% of the cation sites are vacant (as required by valence balance and stoichiometry). A group of distinguished investigators recently demonstrated (3) that the distribution of these vacancies controls surface reconstruction. They also demonstrated that  $\gamma$ -alumina has lower surface energy than  $\alpha$ -alumina so that the transformation process is a competition between bulk volumes and surface areas. This presentation will demonstrate how the combination of advanced analytical techniques such as atomic-resolution Z-contrast transmission electron microscopy and electron energy loss spectroscopy, complemented by x-ray absorption spectroscopy and first-principles theory can be used to identify the role of the promoters in the phase transformation.

This unique understanding of alumina based, catalytic materials is being used to control the exceptional quality of Almatis transition aluminas, like the HiQ<sup>®</sup>-7000 Series Alumina. This control is achieved by linking practical (industrial) processing techniques to the effects of atomic scale processes. In addition, this information is continuously being used to develop new procedures to reduce production costs and improve product quality.

### References:

1. Wefers, K.; Misra, C. Oxides and hydroxides of aluminum. *Alcoa Technical Paper No.19*, Alcoa Laboratories, Pittsburgh (1987).
2. Glazov, M., Novak, J., and Vertegel, A., US Patent 6,764,672, Thermally Stable Alumina Particles (2004).
3. Wang, S., Borisevich, A., Rashkeev, S. Glazoff, M., Sohlberg, K., Pennycook, S., and Pantelides, S., "Dopants Adsorbed as Single Atoms Prevent Degradation of Catalysts," *Nature (Materials)*, vol. 3, 143-146, (2004).

## **Catalytic and Surface Properties of Carbides and Nitrides**

*Levi T. Thompson*

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Since Boudart's discovery of methods to synthesize early transition metal carbides and nitrides with high surface areas, there has been considerable interest in their use as catalysts. These materials have been demonstrated to be highly active for reactions ranging from amination to electrocatalytic hydrogen oxidation to water gas shift. This diversity of function, as well as their performance for selected hydrocarbon conversion reactions has led to comparisons with platinum group metals. This talk will review recent work in our group to understand relationships between the microstructural and catalytic properties of carbides and nitrides, and describe new methods for their synthesis and use as catalyst supports.

## **Chemistry-Aided Design of Future Clean Fuels**

*Edward L. Sughrue and Uday T. Turaga*

Bartlesville Technology Center,  
ConocoPhillips Company,  
Bartlesville, OK 74004

Clean fuels are the result of a continuum of changes in the chemical composition of gasoline and diesel. The removal of lead from gasoline in the 1970s, the addition of oxygenates in the 1990s, and the current removal of sulfur each impacted the chemical composition of fuels. Understanding the interaction between fuel composition and process chemistry enables not only optimal application of current refining processes but also development of new approaches to produce clean fuels. For example, utilizing detailed analyses of the distribution of sulfur-containing molecules in refinery streams, reactor models are now used to both design new hydrodesulfurization units and integrate them with existing units. Similarly, molecular analyses of gasoline streams suggest methods to minimize octane loss during the production of ultra-low sulfur gasoline. These and other examples will be used to discuss the impact of future clean fuel requirements on fuel composition and processing.

**Structure-Function Relationships in Catalysis by Metal Alloys:  
From Single Crystals to Nanoparticles**

*K. Luo, C.-W. Yi, T. Wei, D. Kumar, M.-S. Chen, Z. Yan, Y. Cai, and D. W. Goodman*  
Department of Chemistry  
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College Station, TX 77842- 3012

Model mixed-metal catalysts consisting of Pd alloyed with Au, Cu, and Ag as bulk films on refractory metal single crystals and as nanoparticles supported on oxides have been characterized using an array of surface techniques including X-ray photoemission spectroscopy (XPS), low energy ion scattering spectroscopy (LEIS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED), infrared reflection absorption spectroscopy (IRAS), metastable impact electron spectroscopy (MIES), scanning tunneling microscopy (STM), temperature programmed desorption (TPD), and reaction kinetics. The surface sensitivity of LEIS and IRAS has been exploited for elucidating atomic composition of the outermost surface layer. Of special interest is the composition of the surface compared to the overall composition, particularly in transitioning from planar surfaces to nanoparticles, in the presence and absence of adsorbates. The mechanistic details of the vinyl acetate synthesis reaction, used to probe the structure-function relationship of these alloy surfaces, will also be discussed.

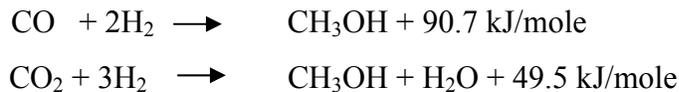
## High Efficiency Reactor for Methanol Production

*Frank Daly*

Velocys, Inc., 7950 Corporate Boulevard, Plain City, OH 43064

Velocys has begun developing a microchannel technology reactor that will greatly intensify the methanol synthesis reaction, thereby making the entire production process more efficient and less costly. When combined with a novel steam methane reformer (SMR) that Velocys is also developing, the resulting process is highly scaleable and can be designed for either low volume, offshore applications or for high volume, land-based facilities

The first step in methanol production is a synthesis gas (syngas) process. Since Velocys' SMR system generates syngas, the current focus is on the second step – methanol synthesis – where syngas is catalytically converted to methanol by the following reactions:



Because both reactions are exothermic and result in a volume reduction, conversion is favored by both low temperature and high pressure. Today's methanol plants are based on a pelletized, copper catalyst that must be operated at 50 atm and temperatures exceeding 210°C to ensure sufficient catalyst activity.

The rate of heat removal in conventional reactors is much slower than the rate of heat release from these exothermic reactions. Additionally, conventional reactors must use pelletized catalysts which have low mass transfer effectiveness factors. Powdered catalysts enable much improved mass transfer rates, but cause excessive pressure drop. Because of these inefficiencies, a low fraction (less than 30 percent) of synthesis gas is converted per pass. Though operating at higher pressure would increase the conversion per pass, the trade-off between capital costs and energy costs has resulted in plant designs with large recycle loops to achieve acceptable yields. Hence, we believe that considerable opportunity exists for developing an improved methanol synthesis process by improving the heat and mass transfer efficiency of the reactor.

Microchannel reactors can greatly increase the per pass conversion for methanol synthesis due to much higher heat transfer rates, catalyst forms with high effectiveness factors, and precise temperature control. Interleaving microreaction channels with heat exchange channels allow for rapid removal of the exothermic heat of reaction generated during synthesis. Additionally, the local temperature can be reduced along the length of the channels. This design enables fast kinetics at the beginning of the reactor to convert the bulk of the syngas into methanol, while favoring equilibrium in the latter stages to achieve superior per pas conversion. These advantages lead to significantly lower capital costs and energy consumption.

For the strongly equilibrium-limited methanol synthesis reaction, the reaction driving force potential is set by local temperature. The Velocys reactor will be hottest at the reactor entrance, and will approach the catalyst highest operating temperature of 270 to 300°C to assist kinetics. The coolest point will be at the reactor exit, and may well be below 200°C or even 180°C to maximize equilibrium driving force potential. A series of isothermal zones control the temperature along the reaction channel. The coolant channel zones have embedded microchannel features which enable partial boiling of water at variable pressures to sequentially decrease temperature.

These systems will have much higher heat and mass transfer performance. Mathematical modeling shows greatly improved per pass conversion with either the commercial available catalysts or improved formulations. By leveraging these advantages, this system could achieve single-pass conversion levels above 80 percent.

Based on the progress with other technology programs, Velocys is collaborating with partnering companies to design, develop, test, and demonstrate breakthrough systems for producing methanol and other chemicals. During the initial phase of each program, the objectives are to design and test a laboratory-scale device, identify promising catalyst formulations, and complete an engineering feasibility studies. During subsequent phases, the primary objectives are to demonstrate an integrated reactor device with an optimized catalyst system, scale-up the technology, complete a detailed engineering evaluation that validates the energy savings and cost advantages, and prepare for commercial demonstration.

## Developing Metal and Metal Oxide Nanoparticles for Heterogeneous Catalysis

Michael S. Wong, William V. Knowles, Michael O. Nutt  
Department of Chemical Engineering, Department of Chemistry  
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With the advances made in solution-phase materials chemistry in the last 20 years, nanoparticles (NPs) can now be prepared out of a wide spectrum of compositions with a high degree of particle size and shape control. NPs are an intriguing class of materials because their reduced physical dimensionality leads to the appearance of catalytic, chemical, optoelectronic, and magnetic properties not found in bulk materials. My group is pursuing two approaches to engineer NPs for catalytic applications, both of which I will present in this talk.

The first approach involves assembling metal oxide NPs into a porous framework that supports another metal oxide, which is achieved through sol-gel processing and surfactant templating chemistry. The resultant material is a supported metal oxide catalyst in which the support domain size is controlled. Interestingly, my group has found that the supported layer to be amorphous at weight loadings above which its crystallization is expected to occur. These NP-supported metal oxides enable the study of thermally stable amorphous metal oxides for gas-phase catalyzed reactions. I will discuss the synthesis and methanol oxidation results for NP-supported  $\text{WO}_x/\text{ZrO}_2$  and  $\text{MoO}_x/\text{ZrO}_2$ .

The second approach addresses the use of unsupported NPs directly as heterogeneous catalysts. NPs can be utilized for liquid-phase reactions provided that the suspension remains stable during the reaction (*i.e.*, the NPs do not precipitate out of suspension) and the NPs can be re-used. My group has been investigating the catalytic activity of Pd NPs and other forms of Pd metal for the aqueous-phase, room temperature hydrodechlorination of trichloroethylene, a reaction that is highly relevant in the environmental remediation of groundwater. We found that NPs comprised of Pd atoms supported on a gold core (~10 nm) are significantly more active than Pd NPs, Pd/alumina, and Pd black. Here, I will discuss the synthesis and trichloroethylene hydrodechlorination catalytic results for Pd-on-Au NPs.

*Dr. Michael S. Wong is currently an assistant professor in the Department of Chemical Engineering at Rice University, with a joint appointment in the Department of Chemistry. Prior to his arrival in 2001, he was a post-doctoral research associate in the Department of Chemistry and Biochemistry at University of California, Santa Barbara. He received a B.S. (1994) in Chemical Engineering from Caltech, an M.S. (1997) in Chemical Engineering Practice from MIT and a Ph.D. (2000) in Chemical Engineering from MIT, with a minor in Materials Science and Engineering.*

## **Oxydehydrogenation of Propane over FeVAl Oxides**

*Dr. Shahid Shaikh*

SABIC Technology Center  
Sugar Land, TX 77478

Mixed FeVAl Oxide is shown to be a very active but low selectivity catalyst for oxidative dehydrogenation of propane, due to large amount of weakly bound lattice oxygen. Addition of Mg, Co, Cr, and Bi enhances the selectivity to propylene, with Bi addition holding most promise to achieve high selectivity and considerable conversion at relatively low temperatures. The reaction pathway on BiFeVAl oxide catalyst proceeds by propane oxydehydrogenation yielding propylene as the exclusive primary product at short contact times. The reaction is first order in propane and 0.2 order in oxygen; that is consistent with a redox mechanism, suggesting the involvement of catalyst lattice oxygen. At longer contact times propylene oxidizes to carbon oxides, reducing the selectivity.

## **Combined Deep Hydrogenation and Ring-Opening of Poly-aromatic Hydrocarbons for Diesel Quality Improvement**

*Daniel E. Resasco\**, *Phuong Do*, *Malee Santikunaporn*, *Roberto Santana*, *Walter E. Alvarez*,

(1) University of Oklahoma, Norman, Oklahoma and

(2) ConocoPhillips, Bartlesville, Oklahoma

The removal of poly-nuclear aromatics from diesel fuel in response to increasingly stringent environmental legislation has stimulated intense research. Deep hydrogenation can greatly enhance the quality of diesel fuels. However, this process alone may not be enough to meet future cetane number targets. As a result, acid-catalyzed ring opening of the naphthenic rings has been proposed in several articles as an interesting addition to the hydrogenation process. Our studies have demonstrated that this is an over-simplification of a more complex problem.

We have investigated this possibility, paying special attention to the different product distributions that can be obtained from different catalysts, acid zeolites and supported metals. We have concluded that there are two types of selectivities in ring-opening, which have not been properly addressed in previous investigations. One selectivity is in regards to the molecular weight; this is obviously necessary to minimize diesel yield losses. The second selectivity is regarding the specific cetane number of the various molecules that result in the ring-opening reaction. It is not obvious that ring opening increases the cetane number. By combining the evaluation of a large number of experimental cetane determinations with predictions conducted via neural network analysis we have demonstrated while n-parafins certainly have a high cetane number, isoparaffin, and one-ring molecules that are produced by ring opening on zeolites have in fact cetane numbers that are not much higher than those of the initial naphthenic molecules (e.g. decalin)

From this analysis, we propose a molecular engineering approach by which we determine what specific chemical bonds need to be opened to maximize cetane number. We will discuss this approach and will describe how we propose to combine hydrogenation with acid-catalyzed ring contraction reactions followed by metal-catalyzed selective hydrogenolysis.

## Ionic Liquid Research in the Petrochemical Industry

Christian P. Mehnert

ExxonMobil Chemical, Baytown Technology and Engineering Complex, Baytown, TX  
christian.p.mehnert@exxonmobil.com.

Ionic Liquids have attracted significant attention in the chemical industry over the last five to ten years. Several novel catalysis and separation processes have been investigated in which ionic liquids have been used as alternative liquid media. The presentation will focus on different aspects of hydroformylation [1] and hydrogenation [2] catalysis, as well as aldol condensation reactions [3] carried out in ionic liquid media.

Furthermore, the concept of supported ionic liquid catalysis [4] will be introduced. In this novel support approach a homogeneous catalyst is dissolved in a multiple layer of an ionic liquid which is confined on the surface of a heterogeneous support (Fig. 1). The ionic liquid layer serves as a liquid phase in which the homogeneous catalyst is dissolved. Although the resulting material is a solid, the active species is dissolved in the confined ionic liquid phase and performs like a homogeneous catalyst.

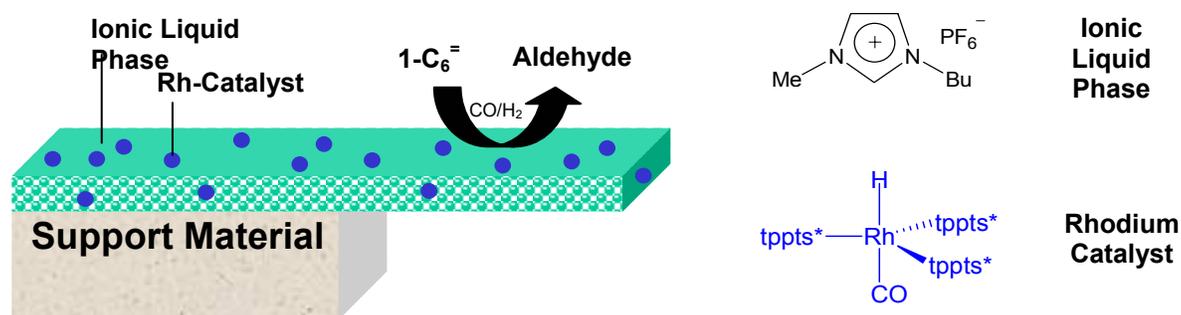


Figure 1. Active complex is immobilized in a multiple layer of ionic liquid on the surface of a heterogeneous support material.

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## **Production of Clean Fuels**

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The future outlook on fuels demand and current regulation will be discussed. The use of new generation catalysts for complying with the new ULSD specifications for grass roots and revamped diesel units is presented. The production of ultra low sulfur gasoline by pre-treating of the FCC feed or post-treating the gasoline pool is discussed.

## Novel Supports for immobilization of MP-11.

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### **Introduction**

Microperoxidase-11 (MP-11) is the product of the proteolytic degradation of cytochrome c. MP-11's usefulness arises from its ability to reduce hydrogen peroxide to water while oxidizing a substrate. However, free MP-11 has the tendency to aggregate in solution due to both intermolecular attraction and ligation through the metal center. When it oligomerizes through coordination to the metal center the heme becomes less accessible and the activity of the enzyme is adversely affected. Immobilization in a suitable material prevents aggregation and makes the heme more accessible to substrate molecules. For the first time we have successfully immobilized MP-11 into mesoporous molecular sieves and a nano-crystalline metal organic framework [Cu(OOC-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-COO) \* 0.5 C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>]<sub>n</sub>.

## Use of Single-Walled Carbon Nanotubes for Fuel Cells

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Fuel cells show great potential to improve energy efficiency, reduce emissions, and reduce noise pollution. Hydrogen and methanol fuel cell systems are the two most often cited as showing numerous advantages. Important developments have been achieved during the last few decades in the development of hydrogen fuel cells and, to a lesser extent, methanol fuel cells. Despite these advances, critical barriers still exist preventing the widespread implementation of either system. Both types of fuel cells rely on platinum or platinum alloy electrocatalysts, and the relatively high precious metal loadings required to achieve acceptable electrode kinetics translate into unacceptably high costs. Because of the high cost of Pt, minimization of the amount of Pt used, while keeping high hydrogen and oxygen conversion rates, is the most wanted objective. It has been suggested that the carbon support not only helps to achieve high Pt dispersion, but also its interaction with Pt may be playing an important direct role in the electrocatalytic process, thus improving the overall fuel cell performance. Recently, it has been shown that the use of carbon nanotubes as the Pt support results in a significantly better electrode performance than when using conventional commercial carbons. Obviously, the current price of SWNT (higher than that of Pt) has discouraged many people to consider this possibility. However, at the University of Oklahoma we have unique capability to produce single-walled carbon nanotubes with closely controlled properties in large scale at a relatively low cost. While the cost of SWNT will go down as the nanotube market develops and SWNT are produced in ton quantities, the price of Platinum is expected to remain at similar values. The performance of platinum-based electrocatalysts is typically compromised by several factors. Cathode kinetics, for example, usually hinders the overall performance of the hydrogen fuel cell, and methanol fuel cell performance is hindered by slow kinetics at both the anode and the cathode. Both types of fuel cells require a mechanically stable, highly proton-conducting polymer electrolyte membrane (PEM), but current materials have significant limitations. Saturation with liquid water, limiting operating temperatures to somewhat less than 100 °C at atmospheric pressure. At this low temperature, CO poisoning is problematic for platinum electrocatalysts, heat removal is made difficult, and electrode kinetics are relatively slow. In the case of direct methanol fuel cells, an additional membrane issue is methanol crossover from the anode side to the cathode caused by high methanol solubility in the membrane material. We believe that single-walled carbon nanotubes show great potential to overcome all of the above critical electrode properties, at least under some conditions. In this work, we present preliminary results obtained using single-walled carbon nanotubes (SWNT) as the support for Pt in the reaction layer.

**THE HYDROGEN EFFECT ON A DINUCLEAR RHODIUM HYDROFORMYLATION CATALYST:  
MECHANISTIC IMPLICATIONS**

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Variation of the H<sub>2</sub>:CO ratio for the hydroformylation of 1-hexene using our dirhodium hydroformylation catalyst, [Rh<sub>2</sub>H<sub>2</sub>(μ-CO)<sub>2</sub>(et,ph-P4)](BF<sub>4</sub>)<sub>2</sub>, in 30% water-acetone solvent leads to linear to branched (L:B) regioselectivities of over 150:1 when the H<sub>2</sub>/CO ratio reaches 4:1. Catalytic studies with ratios between 1:1 and 4:1 will be presented for this and several standard monometallic RhP<sub>2</sub> catalyst systems. Important implications concerning the mechanism of our catalysis will be discussed.

## Hydrogenation Reactions in Catalyst Monoliths

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We are investigating gas/liquid catalytic hydrogenations in typical monoliths, but using novel techniques to control flow and wetting behavior. One such technique is the use of “active focusing”, low frequency, low amplitude oscillations generated by a flexible membrane or piston below the reactor. Such an arrangement can be used in either cocurrent or countercurrent flow, and can operate at high gas/liquid volumetric ratios (typical of a trickle bed) without flooding, unlike a conventional monolith reactor. Initial results have shown an order of magnitude improvement for gas to liquid mass transfer for the air/water system at <20 Hz frequency and <5 mm amplitude. The pulsing action also more evenly distributes gas flow in the monolith channels, even at gas/liquid loadings that lead to hydrodynamically unstable flows in traditional monolith reactors. This development should significantly improve the surface wetting behavior of the catalyst, leading to better selectivity control. By being able to operate at much higher gas/liquid loadings than conventional monolith reactors, we can reap the benefits of such reactors (higher efficiency) over a wider range of operating conditions characteristic of most catalytic hydrogenations.

For initial studies on  $\alpha$ -methylstyrene hydrogenation (a typical test reaction for trickle beds), we have prepared Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> washcoat/cordierite monolith catalysts. The reproducibility of washcoat loadings and thickness was studied. Washcoat thicknesses from 50-300  $\mu$ m could easily be controlled by adjusting the slurry solids content or by performing multiple dipcoats. The high solids content slurries (25-35 wt%) are much more stable when the pH is kept below 5.0, and the slurry is ball milled to below 2  $\mu$ m just prior to coating. Elemental analysis (SEM-EDX) confirmed the lack of impurities in the porous washcoat (250 m<sup>2</sup>/g). Palladium was deposited onto the washcoat by either ion exchange (IX) or incipient wetness impregnation (IWI). Analysis of the catalysts by ICP-AES and H<sub>2</sub> chemisorption showed that IX generally provided a higher dispersion (70%) than IWI, but only allowed for maximum Pd loadings of ~1 wt%, while IWI could give loadings up to 5 wt%.

## The Structure of Catalytically Active Gold on Titania

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The high catalytic activity of gold clusters on oxides has been attributed to structural effects, including particle thickness and shape, metal oxidation state, as well as to support effects. We have created well-ordered gold monolayers [(1x1)] and bilayers [(1x3)] that completely wet (cover) the oxide support [a titanium oxide monolayer film grown on the Mo(112) surface], thus eliminating particle shape and direct support effects (*M. S. Chen, D. W. Goodman, Science 306 (2004) 252; Published online 26 August 2004; 10.1126/science. 1102420*). High-resolution electron energy loss spectroscopy (HREELS) and CO adsorption confirm that the Au atoms are bonded to Ti atoms with slightly negative charge. Ti atoms bound with Au atoms were found to be oxidized from 3+ to 4+ by HREELS and X-ray photon spectroscopy (XPS). It was demonstrated that the bonding of Au-Ti<sup>4+</sup> is stronger than that of bulk Au-Au by temperature-programmed-desorption (TPD). The wetting of Au on the titanium oxide film was also evidenced by our scanning tunneling microscopy (STM) and low-energy ion scattering (LEIS) studies. Kinetic measurements for the catalytic oxidation of carbon monoxide show that the Au bilayer structure is significantly more active (by more than an order of magnitude) than the monolayer, and is about 45 times higher than that reported for the most active higher-surface-area Au/TiO<sub>2</sub> catalyst. These specific rates measured for the Au-(1x3) bilayer structure agree closely with the rates reported previously for Au clusters supported on TiO<sub>2</sub>(110) where an activity maximum was observed for Au structures with two atomic layers in thickness (*M. Valden, X. Lai, D. W. Goodman, Science 281, 1647 (1998)*).

## **NO<sub>x</sub> Storage and Reduction Studies on Pt/Ba/Alumina Monolithic Catalysts**

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Stricter emission standards and the increased use of lean-burn engine technology has prompted the research and development of NO<sub>x</sub> storage and reduction (NSR) or “NO<sub>x</sub> trap” technology. During the NSR process, NO<sub>x</sub> is oxidatively adsorbed on an alkali earth oxide (barium oxide), forming a surface nitrate. The nitrate is then chemically reduced over a noble metal (Pt) by periodic “rich” operation, which increases the level of hydrocarbons in the exhaust, promoting the release and reduction of NO<sub>x</sub>.

The focus of our research has been to systematically investigate the performance of a series of Pt/BaO/Al<sub>2</sub>O<sub>3</sub> monolithic catalysts with varied Pt and BaO loadings. Our objective is to gain insight into the effect of various operating parameters and catalyst compositions on the productivity of the monolithic reactor. Experimental results showed significant enhancement in time-averaged NO<sub>x</sub> conversion was achieved through the intermittent addition of short, intense pulses of reductant into a stream containing NO<sub>x</sub> and excess oxygen.

An extensive study of the NO<sub>x</sub> storage cycle has been performed for the series in order to gain insight into the NO<sub>x</sub> storage mechanism. It was determined that increases in the BaO loading led to increases in the NO<sub>x</sub> storage, but the extent depended upon the exposure time. The effect of increasing the Pt loading on the NO<sub>x</sub> storage was not as clear. Experiments on the Pt series (fixed BaO loading, varied Pt loading) confirmed that the NO oxidation rate is critical to NO<sub>x</sub> storage. The experiments also confirmed that NO<sub>2</sub> can be directly adsorbed to form barium nitrates according to a disproportionation reaction involving the evolution of NO. However, in the presence of both excess oxygen and Pt it is suggested that an alternate storage path that does not involve the evolution of NO exists.

The impact of the catalyst composition under cycling conditions was also evaluated. Increases in Pt loading led to monotonic increases in time-averaged NO<sub>x</sub> conversion during periodic operation, whereas increases in BaO loading did not. Transient concentration profiles were analyzed in order to gain insight into the role of Pt in the overall NSR process, and the role of the Pt-BaO interaction has been examined in order to determine the influence of possible “spill over” reactions. The relationship between the NO<sub>x</sub> trapping efficiency and time-averaged NO<sub>x</sub> conversion was also reviewed.

## Synthesis Of Vinyl Acetate Over Pd Catalysts

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The synthesis of vinyl acetate (VA) has been studied using a variety of catalysts ranging from a low surface area Pd(100) single crystal to high surface area SiO<sub>2</sub> supported Pd and PdAu alloy catalysts with particle sizes ranging from 4.0 to 2.5 nm. The apparent activation energy increases with a decrease in the Pd particle size, varying from 14.0 kJ/mol over Pd(100) to 17.0 kJ/mol over 4.0 nm sized Pd particles to 39.0 kJ/mol for 2.5 nm Pd particles. The VA formation rate increases with a decrease in particle size. On the other hand, the Pd particle size has little effect on the reaction orders with respect to ethylene (negative) and oxygen (positive). The addition of Au to Pd leads to a pronounced increase in the VA reaction rate. Using model catalysts with surface analytical techniques combined with kinetic studies on realistic supported catalysts promises new insights into our understanding of the origins of the high selectivity exhibited by Pd-Au alloys for VA synthesis.

## **Pd-Au Model Catalysts: From Planar Surfaces to Nano-clusters**

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Technical catalysts frequently contain two or more metals, yet much remains to be understood regarding the structure-function relationship in mixed-metal systems. The Pd-Au bimetallic system, used in numerous applications including vinyl acetate synthesis and selective CO oxidation, has been chosen as a prototypical alloy catalyst for our studies. To address the essential features of this alloy system, Pd-Au mixtures have been deposited via physical vapor deposition onto Mo(110) substrates as thin films and onto SiO<sub>2</sub> thin films as nano-clusters. The surface composition of each was determined by ion scattering spectroscopy (ISS), infrared absorption spectroscopy (IRAS), temperature programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS), and the results compared with the corresponding bulk composition. Significant Au enrichment was found for the planar surfaces and nano-particles following a 800 K anneal. An isolated Pd site, characterized by a unique IRAS CO vibrational feature, is proposed as an active center for selective oxidation catalysis. The surface concentration of this isolated Pd site can be controlled by systematically altering the Pd/Au ratio and the annealing temperature. Kinetic and spectroscopic studies are currently underway to explore the role of this isolated Pd site in VA synthesis and CO oxidation.

# Novel Combustion Synthesis and Structural Characterization of Nano-Perovskites Powders

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Complex composites such as  $\text{LaBO}_3$ , (where B = Ga, Fe, Al, or Co) perovskites are widely used oxides with widespread applications in different scientific and industrial fields, including catalysis, electronic devices, and pigments. The properties of some perovskites exhibit high mixed electronic and oxygen ionic conductivities, and for this reason are being widely studied for applications in oxygen separation membranes, chemical sensors and solid oxide fuel cells. Reducing the particle size of perovskites to nanometric scale improve surface activity and physical properties of these materials. There are different methods to synthesize these oxides including conventional solid-state method, self-propagating high-temperature synthesis, laser induced pyrolysis and several wet chemical techniques. However, it remains a challenge to synthesize high selectivity, monophasic and nanosize powders of different compositions using economically and efficiently process. To solve the problems encountered with these complex oxides, efforts are mainly focused on new synthesis routes, which tend to modify.

We have developed the novel carbon combustion synthesis of oxides (CCSO) which is energy efficient one-step technique to produce crystalline, nanosize powders with desired composition. The basic principle of this synthesis is the exothermic reaction between carbon and oxygen, ( $\Delta H = -393.5 \text{ kJ/mol}$ ), which provides the heat for the solid oxide precursors reactions and heats up the adjacent reactant layer. It generates a self-sustaining temperature wave up to  $1200^\circ \text{C}$  that propagates through the reactant mixture. The combustion features such as maximum combustion temperature, front velocity and product properties may be adjusted by the amount of carbon in the reactants mixture. The high rate of  $\text{CO}_2$  release increases the porosity of the particles and the friability of the synthesized powder. All the samples prepared by this approach had high purity perovskite phase with constituted of agglomerated nanometric (50-100 nm) particles.

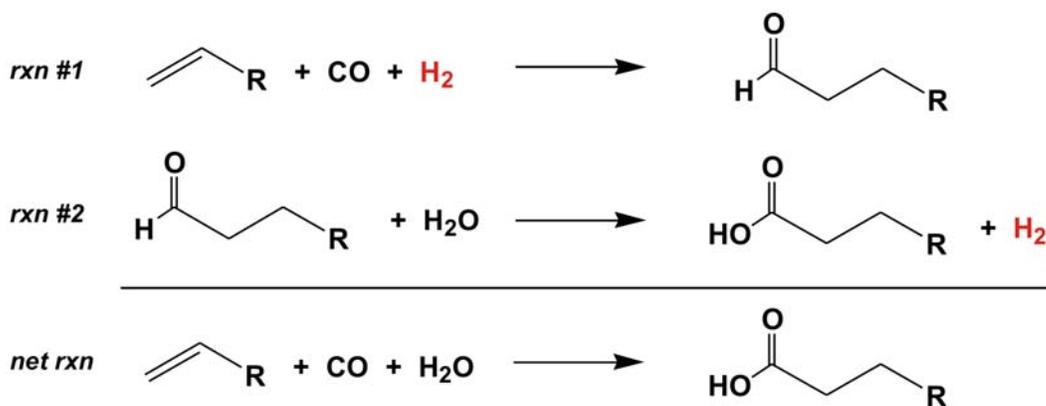
## Hydrocarboxylation of 1-Alkenes via a Tandem Catalysis Reaction using a Tetraphosphine Di-rhodium Catalyst System

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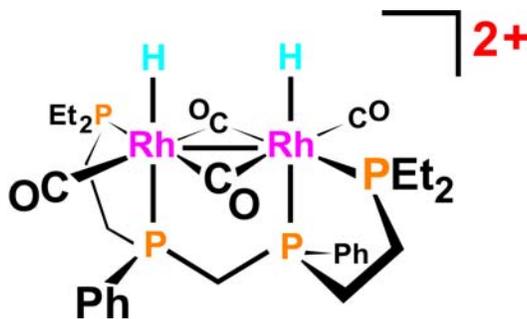
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The dicationic dirhodium tetraphosphine catalysts generated *in situ* from [rac-Rh<sub>2</sub>(nbd)<sub>2</sub>(et,ph-P4)](BF<sub>4</sub>)<sub>2</sub> (nbd = norbornadiene, et,ph-P4 = Et<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(Ph)CH<sub>2</sub>P(Ph)CH<sub>2</sub>CH<sub>2</sub>PEt<sub>2</sub>) and H<sub>2</sub>/CO in acetone/water solvent gives rise to a remarkable tandem catalysis reaction leading to the highly regioselective production of carboxylic acids from 1-alkenes and the generation of H<sub>2</sub> gas. This system operates initially via hydroformylation and then, under H<sub>2</sub>-depleted conditions, converts to an aldehyde-water shift catalysis system producing carboxylic acid and H<sub>2</sub>. This represents one of the most unique and dramatic examples of hydrocarboxylation under very mild reaction conditions (90°C, 6.2 bar H<sub>2</sub>/CO).

### Tandem Catalytic Reactions



### Hydrocarboxylation



Proposed structure for the active hydroformylation catalyst.

## **Zeolite and Metal Oxide Catalysts for the Production of Dimethyl Sulfide and Methanethiol**

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Methanol and H<sub>2</sub>S react in the presence of a metal oxide or zeolite catalyst at 613-673 K to produce dimethyl sulfide (DMS) along with methanethiol (MT), dimethyl ether (DME), and hydrocarbons. Desired products are DMS and/or MT. Aside from activity/cost ratio, minimal formation of methane and other hydrocarbons and resistance to deactivation at optimal H<sub>2</sub>S/methanol ratios are all necessary catalyst characteristics. Mashkina et al. suggested that the most active and selective metal oxide catalysts have both strong Lewis acid sites and moderately basic sites [1]. Both H<sub>2</sub>S and methanol dissociatively adsorb in the presence of these sites, while only methanol can be activated by Bronsted acid sites. Mashkin et al. proposed a serial mechanism in which MT is formed initially and then reacts with methanol to produce DMS [2]. DME is also formed, and it can react with MT or H<sub>2</sub>S to produce S-containing products. Zeolite catalysts such as H-MFI are very active and selective for DMS production at low conversion [3]. Ziolk et al. found that the more acidic zeolites were more active and selective but also deactivated faster [4].

We have tested several metal oxides and zeolites for the condensation of methanol and H<sub>2</sub>S. Methanol was metered into 12% H<sub>2</sub>S/N<sub>2</sub> and flowed through a fixed bed reactor. We found that a supported WO<sub>3</sub> catalyst could be optimized for high MT yield, while La<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> was the most active catalyst tested for DMS production (673 K, stoichiometric feed ratio, WHSV ~ 1.6), and was also very selective (88% yield). The La<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst showed negligible deactivation after 60 h on stream. Reaction pathways will also be discussed – e.g., we found that DME can be converted to DMS under certain conditions, and therefore can be recycled.

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## X-Ray Absorption Spectroscopy of Catalysts for Methylketone Manufacture

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The aim of this work is to determine electronic structure and coordination environment of Ce and dopant atoms in pure and doped (K, Co, Pd) mixed metal oxide catalysts used for the manufacture of methylketones by acid/acid and acid/aldehyde condensations. XANES and EXAFS spectra were collected at room temperature and 420°C (a typical reaction temperature), in both inert and reducing (H<sub>2</sub>) environments. Synchrotron radiation emitted by the Electron storage ring of the Center for Advanced Microstructure and Devices (CAMD) in Baton Rouge running at 1.3 GeV with an average current of 100mA was used. Transmission spectra were taken by pressing the catalyst samples into self-supporting wafers, and then loading them into a controlled atmosphere cell. Normalized XANES data were fitted with model functions to describe the two white lines originating from Ce(IV) at 5728 eV and 5736 eV and the single white line originating from Ce(III) at 5725 eV.<sup>1</sup> From such functions, the ratio of Ce(III) to Ce(IV) is estimated from the peak area ratio. The presence of two white lines at the Ce(IV) edge is ascribed to a mixed valence state of Ce, which consists of a superposition of f<sup>0</sup> and f<sup>1</sup>L states, where L is a hole in the ligand band.<sup>2</sup> In addition to these two lines, a shoulder is present about 4 eV below the first line that is thought to arise from crystal field splitting of the Ce d orbitals by the oxygen coordination shell. The CeO<sub>x</sub> phase in the working catalyst consists of the CeO<sub>2</sub> lattice with oxygen vacancies. These vacancies, combined with the proximity of dopant atoms, alter the initial state mixing of nearby Ce as well as the crystal field splitting of the d orbitals. Such complications make interpretation of XANES spectra difficult.

Nevertheless, it was noted that the Co-doped catalyst (0.8% Co/17% CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) which showed higher yields to methylketones in condensation reactions was also the catalyst with the most oxygen vacancies at 420°C according to the analysis. XANES spectra taken at the Co K edge show a main peak at 7728 eV and a shoulder about 5 eV lower in energy. The main peak corresponds to the white line in CoO and the shoulder is possibly due to a mixed valence initial state of d<sup>7</sup> and d<sup>8</sup>L configurations.

The EXAFS data were analyzed by fitting the Fourier transformed k-weighted spectra (2 – 9 Å<sup>-1</sup>) to theoretical models of possible coordination environments. The spectra of the Co-doped catalysts could not be adequately fit by a linear combination of standards' (Co, CoO, Co<sub>3</sub>O<sub>4</sub>) spectra, nor could they be fit by a theoretical spectrum of a single Co atom doped into a CeO<sub>2</sub> lattice. This suggests that Co is dispersed in CeO<sub>x</sub> as small aggregates.

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## Gas Phase Kinetic Studies of Tetralin Hydrogenation on Pt/Alumina

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Hydrogenation of aromatic compounds present in diesel fuel is a reaction of relevance in the improvement of diesel fuel quality. In this contribution, the kinetics of tetralin (1,2,3,4-tetrahydronaphthalene) hydrogenation over Pt/Al<sub>2</sub>O<sub>3</sub> catalysts has been studied in an integral fixed bed reactor at 500 psig in the temperature range 553-573 K. A semi-empirical Langmuir-Hinshelwood equation has been used to model the kinetics. Three simultaneous reactions were considered in the kinetic model (1) hydrogenation of tetralin to cis-decalin (2) hydrogenation of tetralin to trans-decalin, (3) reversible isomerization of cis- to trans-decalin. The values of the kinetic parameters were determined by a nonlinear fitting using the Powell variant of the Levenberg-Marquardt method, while the heats of adsorption for the hydrocarbons involved (tetralin, cis- and trans-decalin) were experimentally obtained by temperature programmed desorption.

The resulting kinetic parameters obtained from the fitting follow the expected Arrhenius law and meet acceptable physical-chemical criteria and can be used to give a physical explanation of the observed effects. The adsorption competition between tetralin and the hydrogenated products (cis- and trans- decalin) for surface active sites can be quantitatively traced to the higher heat of adsorption of tetralin compared to those of cis- and trans-decalins. As a result, while the activation energy for the cis-trans isomerization is significantly lower than the one for tetralin hydrogenation and its intrinsic reaction rate much higher than that of hydrogenation, the isomerization reaction can only be observed when the concentration of tetralin in the gas phase is very much reduced. In consequence, at low conversions, the trans/cis ratio remains unchanged and it only increases to its equilibrium value at very high tetralin conversions.

## Analysis and Modeling of NO<sub>x</sub> Storage and Reduction in a Monolithic Reactor

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Lean-burn gasoline and diesel vehicles offer a higher fuel efficiency than stoichiometric gasoline vehicles. The lean fuel/air conditions of lean-burn combustion that give the higher efficiency, also produce a net oxidizing exhaust gas containing several pollutants, including VOCs, CO, NO<sub>x</sub>, and SO<sub>x</sub>. Diesel exhaust also includes particulate soot. The long term growth of lean-burn and diesel vehicles depends on how effectively these pollutants can be eliminated from the exhaust. While the net oxidizing exhaust benefits the catalytic oxidation of VOCs and CO, it precludes an effective chemical reduction of NO<sub>x</sub> to nitrogen.

Generally, the NO<sub>x</sub> reduction (conversion) does not exceed 60, due mainly to the oxygen inhibition of NO<sub>x</sub> adsorption and subsequent NO scission and N atom recombination. Thus, the reduction of NO<sub>x</sub> to molecular nitrogen in the exhaust of these engine types is a very important technological challenge.

One of the emerging techniques is that of NO<sub>x</sub> Storage Reduction (NSR), and the device in which NSR is carried out is commonly referred to as the lean NO<sub>x</sub> trap (LNT). The LNT is a periodically-operated adsorptive reactor and comprises a bifunctional catalyst with deliberate periodic operation in which the air fuel ratio is altered between lean (oxygen excess) and rich (fuel excess) mixtures. During the storage phase, NO<sub>x</sub> is incorporated into the alkali earth storage component as a mixture of nitrites and nitrates through a complex set of steps that involve NO oxidation to NO<sub>2</sub> on the precious metal (Platinum), followed by nitration of the alkali earth carbonate, among other pathways. Just before breakthrough of NO<sub>x</sub> in the reactor effluent, a net-reducing mixture is fed to the trap which is accomplished by temporary rich operation of the lean burn engine or by direct injection of reductant (fuel) into the exhaust system. During this regeneration or purge phase the injected hydrocarbon serves the dual role of consuming the excess oxygen and of reducing the nitrites/nitrates. The NO<sub>x</sub> reduction chemistry primarily occurs on the precious metal through a selective catalytic reduction process forming a mixture of nitrogen and N<sub>2</sub>O as the N-containing products. Upon regeneration of the storage component, the feed is switched back to the net oxidizing feed and the cycle is repeated.

A one-dimensional two-phase model of an adsorptive catalytic monolith reactor (used as Lean NO<sub>x</sub> Trap, LNT) is developed and analyzed. The model simulates the features of NO<sub>x</sub> storage and reduction (NSR), a periodic process involving the sequential trapping on a storage component and conversion of NO<sub>x</sub> to nitrogen under lean conditions found in the exhaust of lean burn and diesel vehicles. The effect of design and operating parameters, such as the lean and rich times and feed temperature, on NO<sub>2</sub> conversion is examined. Using a relatively simple kinetic model and without any attempt to fit data, the LNT model predicts the dependencies of NO<sub>2</sub> conversion on several feed parameters that are in good agreement with experimental observations.

## Design of a Sinter-Resistant, Mixed-Oxide Support for Gold Clusters

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The discovery that Au clusters dispersed on metal oxide supports act as efficient catalysts for a variety of low-temperature reactions has led to a great deal of study, with the hope that supported Au clusters may someday replace the less active catalysts currently in use. However, these gold catalysts are plagued by their tendency to sinter under high temperatures and reaction pressures, leading to a dramatic decrease in activity. By creating a method by which the sintering of the clusters could be reduced or completely stopped, it is hoped that the activity level of the catalysts can be maintained. Here, we present STM results showing the production of a mixed titania-silica support for Au clusters. Depending on the amount of Ti deposited, the  $\text{TiO}_2\text{-SiO}_2$  surface consists of substituted Ti atoms and/or  $\text{TiO}_x$  islands. With deposition of Au onto these  $\text{TiO}_2\text{-SiO}_2$  surfaces (at low and high Ti coverages), the substituted Ti and/or  $\text{TiO}_x$  islands act as Au cluster nucleation sites, leading to a marked increase in the cluster number density compared to the Ti-free  $\text{SiO}_2$  surface. Furthermore, upon exposure of Au clusters nucleated on surfaces with  $\text{TiO}_x$  islands to reaction temperatures and pressures, the clusters do not sinter. These results demonstrate that it is possible to produce a supported Au catalyst where metal agglomeration is significantly inhibited, allowing the unique properties of Au nanoclusters to be fully exploited.

## Density Functional Investigation of a Rhodium-Catalyzed Aldehyde-Water Shift Reaction

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Density functional theory has been employed to study a homobimetallic rhodium-catalyzed aldehyde-water shift catalysis. The GAUSSIAN 98/03 suites of programs were used to investigate the *rac*-[Rh<sub>2</sub>H<sub>2</sub>(μ-CO)(et,ph-P4)]<sup>2+</sup> catalyst system and its role in a new type of bimetallic cooperativity that we believe is playing a critical role in the aldehyde-water shift catalysis to produce carboxylic acids. Studies on the electronic and geometric features of the proposed species in the catalytic cycle provide additional support for the mechanism.

# The Electronic Structural Analysis of Di-nuclear Rhodium Catalysts for Hydroformylation

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Density functional theory has been employed to study homobimetallic rhodium-catalyzed hydroformylation. The GAUSSIAN 98/03 suites of programs were used to investigate the *rac*-[Rh<sub>2</sub>H<sub>2</sub>(μ-CO)(et,ph-P4)]<sup>2+</sup> catalyst system. The crystallographic characterization *rac*-[Rh<sub>2</sub>(CO)<sub>5</sub>(et,ph-P4)]<sup>+2</sup> provides important geometric information on the system to which density functional calculational results are compared. These studies on the electronic and geometric features of the proposed species in the catalytic cycle provide additional support for the mechanism and the concept of bimetallic cooperativity in catalysis.

## **Nanoparticle-supported Metal Oxides: WO<sub>x</sub>/ZrO<sub>2</sub> Acid Catalysts**

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Two ZrO<sub>2</sub> nanoparticle(NP)-supported methods were used to synthesize tungstated zirconia catalysts: NP/surfactant-templating (NPST) and a new sol-gel (SG) approach. These materials were compared to WO<sub>x</sub>-ZrO<sub>2</sub> prepared via impregnation and co-precipitation using Raman spectroscopy and methanol dehydration to observe the structure-property relationship of polytungstates on acidic activity. Two observations directly contradicted established models: first, the sample with highest polytungstate concentration (NPST-600(12.1)) exhibited very low dehydration activity; second, surface density was not found to be the sole predictor of dehydration activity as demonstrated by the SG samples. We conclude polytungstates may not be the (sole) active site for methanol dehydration.

## **Designing Pd-on-Au Nanoparticle Catalysts for Aqueous-phase Trichloroethylene Hydrodechlorination**

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Alumina-supported palladium (Pd) catalysts have previously been shown to hydrochlorinate trichloroethylene (TCE) and other chlorinated compounds in water, at room temperature, and under hydrogen atmosphere. The feasibility of this catalytic technology to remediate groundwater of halogenated compounds can be improved by re-designing the Pd material in order to increase catalytic activity. We synthesized and characterized Pd supported on gold nanoparticles (Au NPs) of different Pd loadings. In all cases, we found that these catalysts were more active than Pd NPs, alumina-supported Pd, and Pd-black (62.0, 12.2, and 0.42 L/gPd/min, respectively). There is a synergistic effect of the Pd-on-Au bimetallic structure, with the material with the highest TCE hydrodechlorination activity (943 L/gPd/min) comprised of Au NPs partially covered by Pd metal. The Pd-on-Au bimetallic catalyst structure provides a new synthesis approach in improving the catalytic properties of monometallic Pd materials. The resulting nanoparticle-based materials should be highly suitable as hydrodehalogenation and reduction catalysts for the remediation of various organic and inorganic groundwater contaminants.

## **Mesoporous Carbon Molecular Sieves from Mesoporous Benzene Silica as Catalyst Support for Fuel Cells**

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Mesoporous carbon molecular sieve was prepared from mesoporous benzene silica (MBS). MBS, which is synthesized using 1,4-bis(triethoxysilyl)benzene and octadecyltrimethylammonium surfactant, is a hybrid mesoporous composite with molecular scale periodicity in the pore walls. MBS also displays a homogeneous distribution of the phenyl rings within the pore walls. To prepare the mesoporous carbon,  $\text{H}_2\text{PtCl}_6$  was introduced into the pores of template free MBS by an incipient wetness process and the resulting MBS/ $\text{H}_2\text{PtCl}_6$  powder was heated under vacuum to  $1150^\circ\text{C}$ . This process produced a mesoporous graphitic framework with surface area of  $\sim 950 \text{ m}^2/\text{g}$  and pore size in the 1.7-2 nm range. These materials were characterized by X-ray diffraction, scanning and transmission electron microscopy and nitrogen adsorption. The electrocatalytic activity of the catalysts under fuel cell operating conditions will also be discussed.