

# SOUTHWEST CATALYSIS SOCIETY (SWCS)

## 2006 SPRING SYMPOSIUM

March 17, 2006

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, Chairman

The 2006 SWCS Spring Symposium will be held on Friday March 17, 2006, 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)

On-site 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 2006 Spring Symposium registration fee is \$40, which includes membership due. 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). Group registration can be accommodated on-site; the group representative is to bring a list of names and email addresses and the appropriate total registration fee.

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  
Chairman, SWCS

## **PROGRAM**

- 7:45-8:15 AM Registration**  
Farnsworth Pavilion, Rice University, Houston, TX
- 8:00 AM Yun-feng Chang, ExxonMobil Chemical**  
Welcoming Remarks – Chairman
- 8:05 AM Professor Enrique Iglesia, University of California, Berkeley, CA**  
Burwell Lecture “Structural Requirements and Pathways in Methane Reactions Catalyzed by Supported Metal Clusters”
- 8:50 AM Dr. Jon G. McCarty, Catalytica Energy Systems, Inc.**  
“Durability of Commercial Combustion Catalysts”
- 9:25 AM Professor Peter Strasser, University of Houston, Houston, TX**  
“Catalysis in Electrochemical Energy Conversion”
- 10:00 AM Dr. George Fitzgerald, Accelrys, San Diego, CA**  
“Speeding Catalyst Development with Molecular Modeling”
- 10:35 AM Coffee Break (sponsored by SASOL North America & Micromeritics)**
- 10:50 AM Professor Bert Chandler, Trinity College, San Antonio, TX**  
“Dendrimer Templates for Supported Catalysts”
- 11:25 AM Dr. Edouard Mamedov, SABIC Technology Center, Houston, TX**  
“Diluted Metal Oxides as Catalysts for Selective Oxidation of Alkanes”
- 12:00 Lunch Break**
- 1:10 PM Professor Chunshan Song, Penn State University, University Park, PA**  
“Recent Advances in Adsorption and Desulfurization and Reforming Catalysis in Hydrocarbon Fuel Processing for Fuel Cells”
- 1:45 PM Dr. Roland Saeger, Prasanna Joshi, ExxonMobil Process Research Lab, Paulsboro, NJ**  
“Compositional Modeling of Refinery Streams and Processes”
- 2:20 PM Professor Victor Lin, Iowa State University, Ames, IA**  
“Gatekeeping Effect: Multifunctional Mesoporous Silica Nanoparticles for Selective Catalysis and Conversion of Bio-based Feedstocks to Biodiesel”
- 2:55 PM Poster Session (supported by ChevronPhillips Chemical; ExxonMobil Chemical ) & Coffee Break (sponsored by Custom Catalytic Solution, La Porte, TX)**
- 4:00 PM Awards for best posters – SWCS business – Information on 20th NACS North American Meeting in Houston, 2006**

**Poster Presentations (confirmed so far)**

1. **Karina Castillo, University of Texas, El Paso, TX**  
"Synthesis and Characterization of MoS<sub>2</sub> Intercalated with 1,2,3,4-Tetrahydroquinoline in Search for Cleaner Fuels"
2. **Karen S. Martirosyan and D. Luss, University of Houston, Houston, TX**  
"Novel, Economic Synthesis of Nano-Crystalline Catalysts for Diesel Emission Removal"
3. **M. S. Chen, Z. Yan, Y. Cai, K. Luo, D. Kumar, W. T. Wallace, C. W. Yi, K. K. Gath, and D. W. Goodman, Texas A&M U, College Station, TX**  
"The Structure of Catalytically Active Gold on Titania"
4. **Alan G. Bussard and Kerry M. Dooley, Louisiana State University, Baton Rouge, LA**  
"Heterogeneous Catalyzed Polymer Hydrogenation in an Extruder Microreactor"
5. **Dheeraj Kumar, M.S. Chen, K. Luo, C. -W. Yi, T. Wei, and D. W. Goodman Texas A&M U, College Station, TX**  
"Active site identification for vinyl acetate synthesis on Pd-based catalysts"
6. **Vinay Medhekar, Vemuri Balakotaiah, Michael Harold, University of Houston, Houston, TX**  
"Experimental Analysis and Mathematical Modeling of NO<sub>x</sub> Storage and Reduction over Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/BaO/Al<sub>2</sub>O<sub>3</sub> Catalyst"
7. **Qingsheng Liu, Jack Lunsford, Texas A&M University, College Station, TX**  
"The Roles of Chloride Ions in the Direct Formation of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> over Pd/SiO<sub>2</sub> Catalysts in a H<sub>2</sub>SO<sub>4</sub>/Ethanol System"
8. **Sharath Kirumakki, Boris Shpeizer, and Abraham Clearfield, Texas A&M University, College Station, TX**  
"Characterization Studies on Porous Ni//SiO<sub>2</sub>-AlO<sub>3</sub> Catalytic System"
9. **Kimberly N. Heck, Michael O. Nutt, and Michael S. Wong, Rice University, Houston, TX**  
"SERS as a potential spectroscopic tool for characterizing aqueous-phase TCE HDC over Pd/Au NP surfaces "

# Structural Requirements and Pathways in Methane Reactions Catalyzed by Supported Metal Clusters

Enrique Iglesia

*Department of Chemical Engineering, University of California at Berkeley  
Berkeley, CA 94720, USA*

Kinetic and isotopic evidence for elementary steps and for the effects of cluster size and supports is provided for  $\text{CH}_4/\text{CO}_2$  and  $\text{CH}_4/\text{H}_2\text{O}$  reforming,  $\text{CH}_4$  decomposition, and carbon filament formation on Rh, Pt, Ir, Ru, Pd and Ni clusters at conditions relevant to industrial practice.  $\text{CH}_4/\text{CO}_2$ ,  $\text{CH}_4/\text{H}_2\text{O}$ , and  $\text{CH}_4$  decomposition turnover rates are limited solely by C-H activation of  $\text{CH}_4$  on essentially uncovered surfaces of metal clusters. Turnover rates are proportional to  $\text{CH}_4$  pressure and independent of the identity or concentration of co-reactants and products.  $\text{CH}_4\text{-O}_2$  reactions occur via sequential combustion-reforming pathways, which give partial oxidation products without a direct mechanistic route for extracting  $\text{H}_2$  or CO before their subsequent reactions with  $\text{O}_2$ .

Turnover rates are similar for  $\text{CH}_4/\text{CO}_2$ ,  $\text{CH}_4/\text{H}_2\text{O}$  and  $\text{CH}_4$  decomposition reactions and increased with metal dispersion on all samples, apparently because of the high reactivity of coordinatively unsaturated exposed metal atoms prevalent on small clusters. Activation energies are similar for reactions of  $\text{CH}_4$  with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and for  $\text{CH}_4$  decomposition on each catalyst, but much higher than for  $\text{CH}_4$  activation on single crystals. These differences do not reflect the titration of very active sites by unreactive carbon, but may arise instead from minority defects on macroscopic crystals, which cannot be maintained on the near-molten surfaces of small metal clusters during catalysis. Supports did not influence turnover rates, except indirectly through their effect on metal dispersion, as expected from the sole kinetic relevance of C-H bond activation steps and their exclusive catalysis by metal surfaces.

The identity and kinetic relevance of proposed elementary steps were confirmed by  $\text{CH}_4\text{-CD}_4$  kinetic isotope effects. Normal isotope effects (1.5-1.8) were measured for  $\text{CH}_4/\text{CO}_2$ ,  $\text{CH}_4/\text{H}_2\text{O}$ ,  $\text{CH}_4$  decomposition, and  $\text{CH}_4$  combustion reactions on Rh, Pt, Ir, Ru, Pd, and Ni clusters, indicating that C-H activation steps control turnover rates in all cases.  $\text{CH}_4/\text{D}_2\text{O}$  and  $\text{CH}_4/\text{H}_2\text{O}$  gave similar rates, indicating that  $\text{H}_2\text{O}$  dissociation and  $\text{H}_2\text{O}$ -derived intermediates are kinetically-irrelevant.  $\text{CH}_4/\text{CD}_4/\text{CO}_2$  mixtures formed  $\text{H}_2$  and CO much faster than  $\text{CH}_{4-x}\text{D}_x$  isotopomers, indicating that C-H bond activation is essentially irreversible; the approach to equilibrium for isotopic exchange and for chemical conversion were identical, indicating that C-H activation is the only kinetically-relevant step. Dihydrogen and water formed from  $\text{CH}_4/\text{CO}_2/\text{D}_2$  reached isotopic equilibrium at all chemical conversions; thus, their respective desorption steps are quasi-equilibrated.  $\text{CO}_2$  and CO reached isotopic equilibrium in  $^{12}\text{CH}_4/^{12}\text{CO}_2/^{13}\text{CO}$  mixtures; thus,  $\text{CO}_2$  dissociation is also quasi-equilibrated. The quasi-equilibrated nature of these steps are consistent also with water-gas shift equilibrium, which as confirmed experimentally on all catalysts at all reaction conditions. These mechanistic conclusions were identical on Rh, Ir, Pt, Ru, and Ni clusters irrespective of the support used to disperse metal clusters. These elementary steps and their kinetic relevance give a unifying mechanistic framework for several  $\text{CH}_4$  reactions previously treated independently and for water-gas shift on these metals.

$\text{CH}_4\text{-O}_2$  reactions were examined at conditions that rigorously excluded transport artifacts. Residence time and competitive reaction studies with  $^{12}\text{CH}_4\text{-}^{13}\text{CO-O}_2$  mixtures showed that  $\text{H}_2$

and CO form via sequential combustion-reforming pathways on Pt, Rh, and Ru catalysts. Combustion turnover rates were limited by C-H bond activation in CH<sub>4</sub>; these rates were much higher, however, than for CH<sub>4</sub> reforming, because chemisorbed oxygen atoms are involved in H-abstraction steps. Stoichiometric reactions of CH<sub>4</sub> with bare and oxygen-covered surfaces confirmed the high reactivity of chemisorbed oxygen in C-H bond activation reactions. The observed effects of cluster size and of metal identity on combustion turnover rates reflect corresponding trends in oxygen binding energy and availability during steady-state combustion catalysis. Vacancy-oxygen (\*-O\*) site pairs, which become available as O<sub>2</sub> is depleted, are even more reactive in C-H bond activation than vicinal oxygen pairs (O\*-O\*), leading to relative kinetic contributions that vary with O<sub>2</sub> concentration and to direct partial oxidation pathways only within a very narrow range of O<sub>2</sub> pressure of limited relevance in industrial practice.

Southwest Catalysis Society  
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## **Durability of Commercial Combustion Catalysts**

**Jon G. McCarty**  
Catalytica Energy Systems, Inc.

### ABSTRACT

Thermal coarsening of combustion catalysts under the conditions required for gas turbine applications has been a primary technical concern since interest in this low emissions technology arose in the 1970s. CESI's Xonon® wash-coated foil technology includes several methods of controlling catalytic wall temperature profiles, but outlet gas temperatures in the range of 825 to 950°C are needed for autothermal ignition of the humid lean fuel/air mixture depending on operating pressure, turbine temperature limits, turbine load, and post-catalyst volume. The coarsening rates of supported PGM strongly depend on temperature, water vapor pressure, redox condition and particle phase (metal or oxide, e.g., supported Pd), and the nature of the support. Various examples of 4000-hr and 8000-hr coarsening investigations will be presented in this presentation.

There is nothing comparable to in-field experience to qualify commercial catalysts, both to magnify known or suspected flaws in design and materials selection and to discover harsh and unforeseen realities of the commercial application. Several in-field operating conditions may impact catalyst durability to a greater extent than hydrothermal coarsening. These include: 1) poisoning by air-borne, fuel-borne, and substrate material contaminants; 2) cohesive/adhesive failure of catalyst coatings aggravated by rapid thermal transients experienced in-engine. Approaches to successfully mitigating these durability issues also will be discussed briefly in the presentation.

Unfortunately technical success with a new technology does not guarantee commercial success. By the end of 2005, Xonon®-equipped Kawasaki M1A-13X gas turbines were installed at three sites in California. Two engines have (or will soon) complete their second 8000+hr guaranteed operating period with these lean-burn catalytic combustion modules. Despite this technical success and a successful full-scale in-engine test with the GE Oil & Gas GE-10 8-MW conducted last summer, CESI is unable to sustain commercial activity with ultra-low emission Xonon® catalyst modules and anticipates discontinuing this product in 2006.

The overall effort to develop ultra-low emissions for lean-burn engines continues unabated however, and catalytic combustion is (in my personal view) likely to play a role in a future commercially-viable technology.

31 January 2006  
Mountain View, California

# **Catalysis in Electrochemical Energy Conversion**

Shirlaine Koh and **Peter Strasser**

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Polymer-Electrolyte-Membrane Fuel Cells (PEMFCs) are clean and efficient electrochemical energy conversion devices. Their performance, cost and durability, however, are currently limited by the characteristics of the Pt nanoparticle electrocatalysts at the anode and cathode. Especially at the cathode, severe kinetic overpotentials (output power losses) occur due to the sluggish rate of adsorption and reduction of molecular oxygen on Pt electrocatalysts.

Understanding the mechanistic details of fuel cell electrocatalytic processes in combination with the identification of more active, cost-effective and corrosion stable fuel cell electrocatalysts therefore continues to be a scientific priority in electrochemical energy science.

We present recent progress and future directions in fuel cell catalysis research: We discuss the benefits and the outcomes of a recent combinatorial and high throughput screening technology and compare our results to computational predictions from first principles. We also address the issue of stability of a nanoparticle electrocatalyst and its in-situ measurement.



# **Speeding Catalyst Development with Molecular Modeling**

**George Fitzgerald**

*Accelrys, Inc., San Diego, CA*

Molecular modeling has reached a point where it can make reliable, quantitative predictions regarding catalyst activity and design. Computational results have been incorporated into experimental protocols by a number of companies resulting in catalysts with higher activity, greater specificity, and lowered by-products. The methods are equally applicable to homogeneous and heterogeneous catalysis.

This presentation will outline the current capabilities of catalysis modeling as illustrated by examples in the design of polyolefin and solid acid catalysis, and in predicting the effects of sulfur poisoning on reaction mechanism.

# Dendrimer Templates for Supported Catalysts

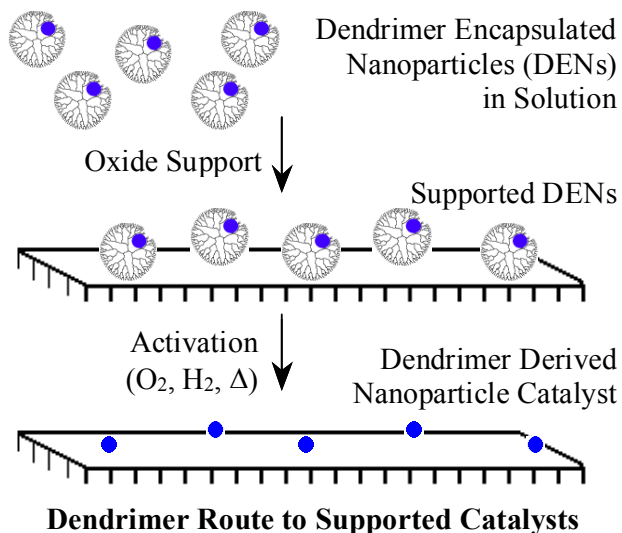
Bert Chandler

*Trinity College, San Antonio, TX 78212*

Polyamidoamine (PAMAM) dendrimers are a class of hyperbranched polymers based on repeating amine - amide moieties. Now commercially available, these architectural motifs have unique three-dimensional macrostructures (porous periphery with an open interior) that make them well suited for trapping and encapsulating guest species, particularly metal nanoparticles. Our research is focused on the application of Dendrimer Encapsulated (metal) Nanoparticles (DENS) to the preparation and characterization of heterogeneous catalysts (see scheme).

DENS offer exciting new opportunities for substantial control over nanoparticle (NP) size and composition in the 1-3 nm size regime.

This size regime is arguably the most important for heterogeneous catalysis as it coincides with the disappearance of a number of bulk metallic properties and the emergence of “nanoscale” or more molecular properties. In particular, dendrimer mediated nanoparticle syntheses offer opportunities for preparing nanoparticle compositions not available via traditional impregnation routes. Recent developments in utilizing DENS as precursors for heterogeneous Pt- and Au-based catalysts will be discussed, along with their potential for studying particle composition and support effects on catalytic test reactions (CO oxidation & toluene hydrogenation).



# Diluted Metal Oxides as Catalysts for Selective Oxidation of Alkanes

Edouard Mamedov

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The paper summarizes the results of comparative studies of bulk and diluted metal oxide catalysts in selective oxidation of C<sub>1</sub>-C<sub>3</sub> paraffins. The bulk catalysts comprised monometal (V<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>) as well as multimetal (VMo, VSb, FeVSb) oxides. The diluted catalysts were prepared by incorporating catalytically inert and low active Mg, Al, Zr, Si, Hf, Ti and Nb to the body of bulk oxides by means of coprecipitation technique. Most of diluted oxides turned out to be more selective catalysts than their bulk analogues. This was the case for methane oxidative coupling on Al-diluted bismuth oxide, propane oxidative dehydrogenation on Al-diluted FeVSb oxide catalyst and propane ammoxidation on VSb oxides diluted with Zr, Al and Mg. Herein, the behavior of diluted oxides depended on the nature of diluent material. The selectivity of propane ammoxidation to acrylonitrile on V<sub>1</sub>Sb<sub>9</sub>M<sub>6</sub>O<sub>x</sub>, where M was diluent, increased at isoconversion in the order VSbNb < VSb < VSbZr < VSbSi < VSbMg < VSbTi < VSbAl. For a given diluent, the extent of dilution was a factor that affected catalyst behavior. With increasing the amount of diluent, both activity and selectivity of VSb oxides passed through the maximum. As a function of the Sb-to-V ratio, activity of diluted catalysts declined with increasing this ratio, while the selectivity increased and then leveled off at a certain Sb/V. Optimized VSbAl, VSbZr and VSbMg oxide catalysts displayed in a wide range of propane conversion essentially higher selectivity to acrylonitrile than corresponding VSb oxide catalysts. In contrast with Mg, Al and Zr, niobium decreased intrinsic selectivity of the VSb oxide catalyst. The positive effect of niobium was that it diminished the overoxidation phenomenon. With increasing propane conversion, acrylonitrile selectivity on Nb-diluted catalyst decreased less than it did on catalysts not containing niobium. Similar effect was observed in oxydehydrogenations of propane and ethane on respectively V<sub>2</sub>O<sub>5</sub> and VMo oxide both diluted with Nb.

Diluted catalysts differed from bulk ones also structurally. Bulk VSb oxides with excess antimony consisted of  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub> and defect rutile phase of approximate composition VSbO<sub>4</sub>. The surface was enriched in antimony that was Sb<sup>5+</sup>. Vanadium was present in the 4+ and 5+ oxidation states. Diluted oxides did not hold rutile or any other vanadium-containing phase. Instead, they contained oxide compounds of antimony with diluent element, such as AlSbO<sub>4</sub>, MgSb<sub>2</sub>O<sub>6</sub> or Nb<sub>3</sub>Sb<sub>3</sub>O<sub>13</sub>, and small amounts of individual oxides of antimony and diluent element. At the surface vanadium and antimony were present as V<sup>5+</sup> and Sb<sup>5+</sup>, and their relative concentrations were close to those in the bulk. It appears that the introduction of catalytically inert or low active element to the VSb oxide promoted the isolation of both vanadium and antimony cations in the structure. This should reduce the number of V – O – V and V – O – Sb chains considered to be degradation sites for hydrocarbons. In the case of bismuth oxide used to activate methane, Bi – O – Bi chains could be responsible for total oxidation. Al-diluted catalyst should have much less such chains since it comprised BiAlO<sub>3</sub>, Bi<sub>2</sub>Al<sub>4</sub>O<sub>9</sub>, Bi<sub>24</sub>Al<sub>2</sub>O<sub>39</sub> phases and no  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> phase. Thus created isolation of bismuth sites was a key factor for obtaining selective catalyst.

Further improvement in behavior of diluted catalysts was achieved by tuning their surface properties. For instance, potassium loaded to the surface of the FeVSbAl oxide significantly increased propane oxydehydrogenation selectivity. This procedure did not change catalyst texture, phase composition and reducibility but decreased surface acidity. Since propane and propylene are considered bases, the increase in selectivity to propylene can be explained by weaker adsorption of both hydrocarbons on less acidic surface that resulted in lower rate of their total oxidation. On the contrary, the selectivity of propane ammoxidation to acrylonitrile was higher on more acidic surface built up by loading VSbAl oxide catalyst with W and Mo. This result looks reasonable because propane ammoxidation on this catalyst occurred via intermediate propylene, which needed to reside on the surface longer time in order to undergo ammoxidation to acrylonitrile. Using similar approach, the selectivity of ethane oxidation to acetic acid on VMoNb oxide catalyst was increased by two times at the expense of selectivity to ethylene.

# **Recent Advances in Adsorption Desulfurization and Reforming Catalysis in Hydrocarbon Fuel Processing for Fuel Cells**

**Chunshan Song**

Clean Fuels and Catalysis Program, The Pennsylvania State University  
University Park, PA 16802

Clean energy has become an important focus of catalysis research worldwide. This lecture will begin with a brief discussion on the global energy challenges in the 21st century, and role of catalysis in hydrogen energy development, followed by a brief overview on role of catalysis in hydrogen production, storage, and utilization. Then the discussions will focus on fuel processing for applications in both high-temperature fuel cells (SOFC, MCFC) and low-temperature fuel cells (PEMFC and PAFC). Hydrocarbon fuels and alcohol fuels can both be used as fuels for reforming on-site or on-board. Alcohol fuels can be reformed at lower temperatures, but hydrocarbon fuels have the advantages of existing infrastructure of production and distribution. Further research and development is necessary on fuel processing for improved energy efficiency and reduced size of fuel processor. More effective ways of deep removal of sulfur before or after fuel reforming, and more energy-efficient and stable catalysts and processes for reforming hydrocarbon fuels are necessary for fuel cells. Recent research in our laboratory will be presented on selective adsorption for removing sulfur (PSU-SARS) before and after reforming, on sulfur-tolerant and carbon-resistant catalysts for reforming of liquid hydrocarbon fuels, on low-temperature oxidative reforming of alcohol fuels (MeOH, EtOH), and on oxygen-assisted water gas shift (OWGS) reaction.

More background information for this lecture can be found in some recent reviews [Song, C.S. Fuel Processing for Low-Temperature and High-Temperature Fuel Cells. Challenges, and Opportunities for Sustainable Development in the 21<sup>st</sup> Century. *Catalysis Today*, 2002, 77, 17-50; Song, C.S. An Overview of New Approaches to Deep Desulfurization for Ultra-Clean Gasoline, Diesel Fuel and Jet Fuel. *Catalysis Today*, 2003, 86 (1-4), 211-263].

# Compositional Modeling of Refinery Streams and Processes

**Roland B. Saeger**

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Historically, petroleum streams have been viewed as a mixture of boiling fractions. In reality, these streams are complex mixtures of hydrocarbons containing enormous numbers of distinct molecular species. The streams are so complex, and have so many distinct molecular species that any molecular approximation of the composition is essentially a model, that is, a model-of-composition (MoC). ExxonMobil's High-Detail Hydrocarbon Analysis (HDHA) combines a proprietary liquid chromatographic separation process with other advanced analytical methods. The MoC, containing thousands of molecular lumps, is reconciled to the results of the HDHA protocol. Refinery process models have been developed that simulate physical and chemical transformations at the same level of molecular detail as the MoC. Molecular composition has also been correlated to several physical and performance properties critical to refinery operations.

ExxonMobil uses the composition-based modeling platform described above to optimize its refining business, including feedstock selection. In this talk, we discuss the essentials of the HDHA protocol and reconciliation to a MoC, the Structure-Oriented Lumping (SOL) approach to constructing reaction networks, and give examples of composition-based property correlations. We also discuss the user interfaces that have been constructed to enable seamless integration between MoC feed libraries and SOL-based refinery process models.

# Gatekeeping Effect: Multifunctional Mesoporous Silica Nanoparticles for Selective Catalysis and Conversion of Bio-based Feedstocks to Biodiesel

Victor S.-Y. Lin

*Department of Chemistry and U.S. DOE Ames Laboratory, Iowa State University  
Ames, Iowa 50011-3111*

We have developed a new synthetic strategy for multifunctionalization of mesoporous silica nanoparticle (MSN) materials. This method allows us to tune the relative ratio of different functional groups and the resulting particle morphology of MSNs. By introducing two organoalkoxysilanes as precursors in our co-condensation reaction, we can utilize one precursor with *stronger structure-directing ability* to create the desired pore and particle morphology and employ the *other* for selective immobilization of catalysts. As a proof of principle, we have synthesized and reported a series of bifunctionalized MSN-based heterogeneous catalysts for nitroaldol (Henry) reaction. A common 3-[2-(2-aminoethylamino)ethylamino]propyl (AEP) primary group and three different secondary groups, ureidopropyl (UDP), mercaptopropyl (MP), and allyl (AL) functionalities, were incorporated into these mesoporous silica materials by introducing equal amounts of AEP-trimethoxysilane with UDP-, MP- or AL-trialkoxysilane precursors to the aforementioned co-condensation reaction. The AEP group served as a catalyst and the other secondary groups provided different non-covalent interactions to reactants and thereby controlled the reaction selectivity. By varying the secondary group in these bifunctionalized MSN catalysts, we have discovered that the selectivity of a nitroaldol reaction of two competing benzaldehydes reacting with nitromethane could be systematically tuned simply by varying the physicochemical properties of the pore surface-bound secondary groups, *i.e.* polarity and hydrophobicity.

Furthermore, we have reported a new cooperative catalytic system comprised of a series of bifunctionalized mesoporous silica nanosphere (MSN) materials with various relative concentrations of a general acid, ureidopropyl (UDP) group, and a base, 3-[2-(2-aminoethylamino)ethylamino]propyl (AEP) group. We were inspired by the fact that enzymes engaged in carbonyl chemistry often employ both general acid and base catalytic residues in the active sites to cooperatively activate specific substrates. In this system, we have demonstrated that the general acid group, UDP, could cooperatively activate substrates with the base group, AEP, in catalyzing various reactions that involve carbonyl activation, such as aldol, Henry and cyanosilylation reactions. By further utilizing this approach, we have developed a calcium silicate mixed oxide catalyst that contains both Lewis acidic and basic sites for the synthesis of biodiesel from various free fatty acid (FFA)-containing oil feedstocks. We have demonstrated that the acid and base functionalities could cooperatively catalyze both the esterification of FFAs and the transesterification of oils with short-chain alcohols (e.g. methanol and ethanol) to form alkyl esters (biodiesel). We envision that these multifunctionalized MSNs could serve as new selective catalysts for many other important reactions.

# Synthesis and Characterization of MoS<sub>2</sub> Intercalated with 1,2,3,4 Tetrahydroquinoline in search of Cleaner Fuels

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Sulfur, in high concentrations, has adverse effects on living things and their environment. The EPA (Environmental Protection Agency) has established regulations limiting the amount of sulfur that can be released to the environment when using hydrocarbon fuels. In order to meet these regulations, the hydrodesulfurization (HDS) process is used by refining industries to remove sulfur-containing compounds. MoS<sub>2</sub> based catalysts are widely used for the removal of sulfur from heavy crude oils. The catalytic properties of MoS<sub>2</sub> are controlled by its anisotropic layered structure. Opening of these layers and insertion of organic compounds is a process called intercalation. Synthesis of intercalated organic compounds may lead to improved hydrogenation catalytic properties of MoS<sub>2</sub>. MoS<sub>2</sub>C<sub>x</sub> was synthesized by a three step process: single layers were synthesized by the addition of n-Butyl Lithium, followed by removal of Li by the addition of water and dispersion. The single layers were then restacked with 1,2,3,4 tetrahydroquinoline creating the intercalated compound.

The synthesized compound MoS<sub>2</sub>C<sub>x</sub> was analyzed using Infrared Spectroscopy, Synchrotron X-Ray Powder Diffraction (XRD), <sup>13</sup>C NMR and the Cerius<sup>2</sup> 4.5 simulation software. Infrared spectroscopy showed absorbencies in the near infrared region in contrast with the absorbencies of MoS<sub>2</sub> in the far infrared region. The XRD pattern showed a new reflection corresponding to the plane 001. The XRD reflection at 001 is indicative of a new lamellar compound from the starting MoS<sub>2</sub>. Using the Rietveld Refinement method from the Cerius software, the cell dimensions of the new compound correspond to a monoclinic structure. The cell dimensions are a=5.9, b=3.27, c=13.29,

$\alpha=90^\circ$ ,  $\beta=110^\circ$ ,  $\gamma=90^\circ$ . <sup>13</sup>C NMR after intercalation with THQ still has the peaks at 41.93, 22.7 and 27.7ppm indicating the presence of THQ. This result is indicative that there was not a dehydrogenation reaction at the pyridine ring. However, new peaks arise in the region of 113 to 150 ppm indicate that the THQ was partially dehydrogenated at room temperature. The new compound MoS<sub>2</sub>R<sub>x</sub> (R=THQ and x~0.25) might be a more efficient catalyst for the removal of sulfur in oil refineries.

## The Structure of Catalytically Active Gold on Titania

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The unique catalytic activity of supported Au nanoparticles has been ascribed to various effects including thickness/shape, the metal oxidation state, and support effects. We have synthesized well-ordered Au mono- and bi-layer films that completely wet a  $\text{TiO}_x/\text{Mo}(112)$ , thus eliminating particle shape and direct support effects. The wetting and ordered Au films are evidenced by recent STM studies, as well as LEIS and TPD investigations. The electronic and chemical properties of these ordered Au films have been characterized by IRAS using CO as a probe molecule and UPS, with both techniques indicating the Au overlayers to be electron-rich. Kinetic measurements for the catalytic oxidation of carbon monoxide show that the Au bi-layer 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/ $\text{TiO}_2$  catalyst. The common structural features of ordered Au bi-layers and Au bi-layer nanoparticles on  $\text{TiO}_2(110)$  are described, and the exceptionally high catalytic activity of the Au bi-layer structure related to its unique electronic properties.

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# Heterogeneous catalyzed polymer hydrogenation in an extruder microreactor

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## Introduction

There has been a recent interest in the modification of common polymers as a way to produce new specialty derivatives with minimal additional processing.<sup>1,2,3,4</sup> Both homogeneous and heterogeneous catalysts have been used to hydrogenate polymers.<sup>5,6</sup> However, homogeneous catalysts are often difficult to completely remove from the product. Lack of complete removal can lead to unwanted side reactions such as chain scission.<sup>4,6</sup> Most heterogeneous catalysts for polymer hydrogenation are used as stirred slurry tanks operated in batch mode where the powdered catalyst must still be filtered out of the product.<sup>1,2,3,4</sup> These reactors are also typically operated under low concentrations (<5 wt%) of polymer to avoid gas mass transfer limitations. These limitations have restricted three phase polymer reactions from becoming industrially viable. Here we investigate the use of an extruder as a novel reactor system for the heterogeneous catalyzed hydrogenation of polystyrene (PS) to poly(vinylcyclohexane) (PVCH).

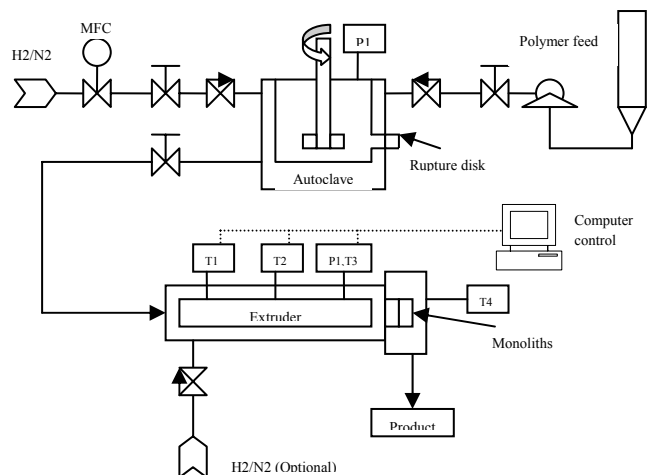
## Experimental

**Materials.** Commercial PS was purchased from Dow Chemical with an average molecular weight of 100,000 (measured from intrinsic viscosity) and was used as received. Cyclohexane (99.9+%) and tetrahydrofuran (99.9+%) were purchased from Fisher and used without further purification. Versal V-250 pseudoboehmite was obtained from LaRoche Chemicals and used as an Al<sub>2</sub>O<sub>3</sub> precursor. The Palladium precursor was purchased from Pressure Chemical as PdCl<sub>2</sub>.

**Preparation of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.** The pseudoboehmite was first calcined by placing in a furnace and ramping the temperature up to 500 °C at a rate of 2 °C/min under flowing air. Ion exchange (IX) was used to add Pd to the alumina support. Both NH<sub>3</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> were added to the solution as their respective forms of NH<sub>4</sub>OH and NH<sub>4</sub>NO<sub>3</sub>. Both ions were added to the solution in amounts greater than their molar ratios in the Pd(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> complex to ensure that all Pd was converted. It was found that a higher pH IX solution was better at affixing the Pd to the support than a lower pH. However, at a pH~12.0, Pd did precipitate out of solution, meaning a pH of ~11 offers the maximum attainable reaction driving force. Because the concentration of PdCl<sub>2</sub> dissolved in aqueous solution was so dilute (0.3g/L), the presence of Cl<sup>-</sup> was found to have a negligible impact on the acidity of the support. This was confirmed by adding 1% AgNO<sub>3</sub> solution to the rinsate and having no precipitate form. It was also found that the IX reaction was improved by mild heating of the alumina/aqueous mixture and stirring overnight. The IX process was repeated two times to increase the loading. The final dried Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder was dip coated onto a 100 cells per square inch (cps) cordierite monolith. Coating thickness was controlled by varying the slurry solids content. The final step was reduction at 130 °C in 10% H<sub>2</sub>/N<sub>2</sub> and raising the temperature to 300 °C in He to burn off any remaining amine ligands.

**Design of the extruder microreactor.** The reactor was a modified Haake Rheocord 9000 which consisted of a controller unit and a drive unit that operated the intermeshing twin screws. A custom made die that held two monoliths was attached to the end of the extruder. Temperature control was provided by 4 independent zones. A transducer provided pressure data at the die inlet. The polymer solution was first pumped into an autoclave at high pressure where hydrogen was pre-dissolved and mixed. Hydrogen flowed to the autoclave through a high pressure mass flow controller to record the flow of gas. The solution was then fed into the extruder inlet where

it was mixed and forced down the extruder barrel and through the catalyst coated monoliths. The liquid was collected at the die exit and the flow recorded. A schematic of the extruder microreactor is shown in **Figure 1**.



**Figure 1.** Extruder microreactor schematic.

## Results and Discussion

**Catalyst Characterization.** TGA results confirm the formation of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase, which is the first transition alumina formed upon complete dehydroxylation. Samples of calcined alumina had a BET surface area of 248 m<sup>2</sup>/g, which is typical of gamma aluminas.

ICP-AES results show the loading after 3 IX steps to be 0.5 wt% Pd. Subsequent IX did not give a higher loading, likely indicating all available hydroxyl surface sites had already reacted with the tetraamine complex. H<sub>2</sub> chemisorption measurements indicated Pd dispersion was very high (~70-80%). Chemisorption was also used to confirm complete reduction had taken place by verifying attempts at further reduction led to no increase in dispersion. SEM results show a thin washcoat is desired to limit the amount of cracking and flaking of the washcoat.

**Reactor Studies.** Initial reactor studies were performed to study the range of gas to liquid volumetric ratios possible by varying the gas supply pressure. At the low end a G/L ratio of 5 was possible at a pressure of 2.4 MPa. The maximum G/L ratio was 20 at a pressure of 3.4 MPa. Reactions have been performed under continuous operation and compared to batch reactor studies using the same catalyst between 150-180 °C. Conversion was monitored using a Jasco V-570 UV-Vis spectrometer and monitoring the aromatic peak at 262 nm. The reaction rate constants modeled from the PFR design equation indicate performance approximately one order of magnitude less than a conventional stirred tank. The most likely reason for this is poor bubble size distribution due to phase separation inside the monoliths as a result of screw flights partially filled with liquid. Future work will concentrate on possible ways to improve bubble breakup inside the monoliths by periodic direct gas injection into the extruder barrel as a way to induce unsteady state flow.

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# **Novel, Economic Synthesis of Nano-Crystalline Catalysts for Diesel Emission Removal**

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The economic removal of carbon particulates (soot) formed by diesel engines is a major unsolved problem. A proposed solution is the use of filters on which a catalytic combustion of the soot is conducted. Use of precious metal catalysts is an expensive solution. A more economic solution is the use of nano-crystalline complex oxides as the catalyst. Several of these have appreciable catalytic activity at 300-400°C for soot oxidation and limited sensitivity to hydrothermal aging. The current productions of these complex oxides nano-particles are relatively expensive. We have recently developed a novel combustion process, named *Carbon Combustion Synthesis of Oxides* (CCSO), for economic production of high-quality complex oxides. It produces oxides much faster (order of minutes) than the common calcination process (order of hours) without any external power consumption and using rather inexpensive raw materials. We used CCSO to produce catalyst materials such as  $\text{Cs}_4\text{V}_2\text{O}_7$ ,  $\text{LiCrO}_2$ , and  $\text{La}_{0.8}\text{Cr}_{0.9}\text{Li}_{0.1}\text{O}_3$  for diesel emission removal. These materials exhibit high catalytic activity and are also CO and  $\text{SO}_2$  - tolerant.

In CCSO the exothermic oxidation of carbon generates a thermal reaction wave (temperature gradient of up to 500 °C/cm) that propagates at a velocity of 0.1-3 mm/s through the solid reactant mixture converting it to the desired oxide product. The major parameters affecting the synthesis and properties of the catalyst are the carbon concentration in the reactant mixture, type of precursors, and density/porosity of sample, which controls the ability of the oxygen infiltration to the reaction zone. The release of carbon dioxide ( $\text{CO}_2$ ) generates many pores and the synthesized powders are friable and loosely agglomerated. The grain size of most products is less than 0.1  $\mu\text{m}$  and the porosity of the products is up to 0.7 with a surface area  $\sim 10 \text{ m}^2/\text{g}$ . XRD analysis and electron probe microanalysis of as-synthesized catalysts show that essentially complete conversion to single-phase products was accomplished during the synthesis.

# Active Site Identification for Vinyl Acetate Synthesis on Pd-based Catalysts

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Vinyl acetate (VA) synthesis over Pd-Au catalysts is an important industrial reaction that has been studied extensively; however, there is no consensus regarding the reaction mechanism, the active site, the key intermediates, and the role of Au. In the present study, a combination of surface science techniques and kinetic measurements has been used to study the details of VA synthesis. On Pd high-surface-area catalysts the reaction rates were found to be: Pd(100) < 5 wt% Pd/SiO<sub>2</sub>( $\bar{d}_{Pd}:4nm$ ) < 1 wt% Pd/SiO<sub>2</sub>( $\bar{d}_{Pd}:2.5nm$ ). Moreover, addition of Au to Pd/SiO<sub>2</sub> catalysts significantly enhances the VA formation rate and slightly increases the selectivity. Infrared reflection absorption spectroscopy (IRAS) of CO on Pd/Au(100) and Pd/Au(111) substantiates the presence of Pd as isolated monomers on a Au-rich surface. A pair of Pd monomers was found to constitute the active sites for VA formation. The spacing between the two active Pd monomers is critical, apparent by the relative rates of VA formation on Pd/Au model catalysts, i.e. Pd/Au(111) < Pd/Au(100). The role of Au is to isolate the surface Pd atoms and thus suppress the formation of by products, CO and CO<sub>2</sub>. A pair of Pd monomers required for VA synthesis is further confirmed by the results from model studies of Sn-Pd.

# Experimental Analysis and Mathematical Modeling of NO<sub>x</sub> Storage and Reduction over Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/BaO/Al<sub>2</sub>O<sub>3</sub> Catalyst

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The NO<sub>x</sub> storage and reduction (NSR) is emerging as a prominent technology for NO<sub>x</sub> emission abatement for lean burn and diesel engines. The NO<sub>x</sub> removal process involves two stages on a bifunctional supported catalyst. The first stage involves storage of NO<sub>x</sub> on an alkali earth component (such as Ba, K) mediated by a precious metal (Pt, Rh). Prior to the breakthrough of an unacceptable amount of NO<sub>x</sub>, the second stage of purging is carried out by a shorter exposure of rich pulse. Elucidation of the synergistic roles played by both alkali compound and precious metal is key in improving the efficiency of the NSR process. In the current study we employ Temporal Analysis of Products (TAP) to probe the catalytic chemistry. The transient TAP protocols (pulsing, pulse-probing) are well suited for the current study since NSR is an inherently transient catalytic process. To this end, we seek to develop a mechanism by conducting systematic TAP experiments together with mathematical modeling and kinetic parameter estimation. Moreover, the TAP enables storage and reduction at essentially a fixed degree of NO<sub>x</sub> storage since pulse size is considerably less than the number of catalytic sites, an experiment difficult to accomplish with other approaches.

To begin with, the catalyst is first reduced in H<sub>2</sub> under varying conditions to have different starting state for the reaction. A fixed number ( $\sim 10^{16}$ ) per pulse of NO molecules are pulsed over different Pt-BaO/Al<sub>2</sub>O<sub>3</sub> catalyst at low pressure of  $\sim 10^{-7}$  Torr and temperature of 300 – 450 °C. The low number of molecules ensures Knudsen diffusion. The products are analyzed using Quadrupole mass spectrometer. To understand the interaction of Pt with Ba for NO storage, we first try to analyze the storage over Pt and Pt-Ba by sending a continuous train of NO pulses. The resultant products show that N<sub>2</sub> is the predominant product for first few pulses that goes through maximum and reduces to zero. The NO decomposition over Pt leaves surface bound atomic O<sub>2</sub> which poisons the catalyst, decreasing the amount of N<sub>2</sub> produced. N<sub>2</sub>O production goes through maximum for Pt/Al<sub>2</sub>O<sub>3</sub> and is reduced to zero while its production is sustained for much longer period over Pt/BaO/Al<sub>2</sub>O<sub>3</sub>. On parallel lines, NO is stored on the Ba component with the help of Pt. When the Ba surface is saturated around Pt sites, we have NO breakthrough in the exit

stream. Subsequent reduction of stored NO<sub>x</sub> with H<sub>2</sub> shows N<sub>2</sub> production with water and ammonia as by-products. We observe that storage of NO occurs in two steps: NO decomposition over Pt followed by spillover of adsorbed O<sub>2</sub> from Pt to Ba to store NO. To understand the complete NSR cycle, we perform NO/H<sub>2</sub> pump-probe experiments, which involves alternate pulsing of NO and H<sub>2</sub>. The advantage of this technique is that we are sending relatively a very low number of molecules compared to catalyst sites for each NSR cycle (thereby not changing the surface of catalyst) so the products observed are purely from the reaction on catalyst. Pump-probe on pre-reduced catalyst surface with H<sub>2</sub>: NO > 1 shows constant production of N<sub>2</sub> during NO pulsing indicating complete regeneration of the surface after every H<sub>2</sub> pulse. In H<sub>2</sub>: NO < 1 over clean surface show gradual poisoning of catalyst. On a pre-nitrated surface with H<sub>2</sub>: NO > 1 show release of N<sub>2</sub> from the stored surface along with production of water and NH<sub>3</sub>. The relative selectivity of the products helps us to understand the mechanism of the NSR cycle.

First principles based mechanistic models that can explain the TAP experiments are developed and the kinetic constants are determined by fitting the model predictions to the TAP data. Our study shows conclusively that Pt and Ba interface plays a significant role in the storage of NO<sub>x</sub> over the catalyst. We also show production of NH<sub>3</sub> on a pre-nitrated catalyst surface in excess of hydrogen. The findings have important implications with respect to optimal catalyst design, safety concerns and aging. These and other issues will be presented

# The Roles of Chloride Ions in the Direct Formation of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> over a Pd/SiO<sub>2</sub> Catalyst in a H<sub>2</sub>SO<sub>4</sub>/Ethanol System

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## Abstract

Hydrogen peroxide is produced directly from H<sub>2</sub> and O<sub>2</sub> over a Pd/SiO<sub>2</sub> catalyst in a slurry of ethanol acidified with H<sub>2</sub>SO<sub>4</sub>. The effects of chloride ions on the reactions involving the formation of H<sub>2</sub>O<sub>2</sub>, as well as the formation of water via the combustion of H<sub>2</sub> and the reduction or decomposition of H<sub>2</sub>O<sub>2</sub>, were investigated by adding small amounts of HCl to the system. In the absence of chloride ions the net rate of H<sub>2</sub>O<sub>2</sub> formation was very small because the combustion reaction was dominant. At a Cl<sup>-</sup> concentration of  $4 \times 10^{-4}$  M the formation of H<sub>2</sub>O<sub>2</sub> proceeded at a reasonable rate with a selectivity of ca. 45 % based on H<sub>2</sub> conversion. During the early stages of the reaction hydrogen was consumed both in the formation of H<sub>2</sub>O<sub>2</sub> and in the combustion reaction, but as more peroxide was formed the reduction of H<sub>2</sub>O<sub>2</sub> became a significant reaction. The positive effect of Cl<sup>-</sup> on the surface Pd appears to result from the inhibition of O–O bond breaking both in dioxygen and in hydrogen peroxide. The former effect limits the combustion reaction and the latter the decomposition and reduction reactions.



## Characterization studies on porous NiO/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalytic system

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A series of NiO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts were synthesized by the sol-gel method. The surface area and pore sizes of these materials can be varied by varying the primary amine used during the synthesis. The samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), H<sub>2</sub>-temperature programmed reduction (TPR) and temperature programmed desorption (TPD) of NH<sub>3</sub>. The nature of Ni species on the support and their interaction with the support has been studied. It has been found that Ni is present as Ni<sup>2+</sup> (NiO) on the support; there is no Ni<sup>3+</sup> or Ni<sup>0</sup> in the unreduced samples. Two types of NiO were identified in these systems, one which has no interaction with the support (free NiO) and the other with interactions with the support. The extent of interaction between the NiO and the support depends on the total Ni content and on the Si/Al ratio of the sample. At high Ni concentrations the metal support interaction is less and there is a relatively large proportion of free NiO. An increase in the SiO<sub>2</sub> content in the support increases the interactions between NiO and the support. The activity of these catalysts in hydrogenation of naphthalene has been correlated with the relative concentration of free NiO present.

## **SERS as a potential spectroscopic tool for characterizing aqueous-phase TCE HDC over Pd/Au NP surfaces**

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The catalytic destruction of groundwater pollutants is an attractive alternative to conventional environmental remediation utilizing displacement or containment, such as air stripping or adsorption by activated carbon. Recently, we discovered that Pd-on-Au nanoparticles (Pd/Au NPs) converted trichloroethene and other chlorinated compounds to ethane up to 70x faster than commercially available Pd supported on Al<sub>2</sub>O<sub>3</sub> (Nutt, Hughes, and Wong, *Environ. Sci. Technol.* 39, 1346-1353, **2005**). During batch reactions of tetrachloroethylene (PCE) and trichloroethylene (TCE) on Pd/Au NPs, small amounts of dichloroethylene (DCE) isomers were observed, which indicated that TCE and PCE generated the formation of desorb-able chlorinated intermediates before complete HDC into ethane. In this poster, we present our current efforts on applying surface-enhanced Raman spectroscopy (SERS) to analyze the nature of adsorbates and reaction intermediates on Pd/Au surfaces. It is known that Au NPs exhibit surface plasmon resonance (SPR) at visible light frequencies. This phenomenon allows chemicals bound to the metal surface to be probed using SERS with commonly available photon sources. Spectra obtained through this method of chemical sensing could be used to determine how TCE and the reaction intermediates bind to the metal surface, by comparing the Raman spectra of the TCE at the catalyst surface versus free TCE.