SOUTHWEST CATALYSIS SOCIETY

2015 SPRING SYMPOSIUM

Friday, April 24, 2015

*Melcher Hall, Room 150
University of Houston, Houston, TX

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The SWCS officers and I welcome you to the 2015 SWCS Spring Symposium, **Friday, April 24, 2015**, at the University of Houston in Melcher Hall, Room 150 (building #528 on the University of Houston map on the back page).

We are delighted to present six invited speakers and **31** poster presentations for this year's meeting. Meritorious posters presented by students and post-docs will be identified with **Best Poster Awards**, carrying cash prizes. The poster session will be held in the first floor atrium of Engineering Building 1 (see the map for details).

The 2015 Spring Symposium **registration fee is $50**, which includes North American Catalysis Society and SWCS annual membership dues, along with coffee/snack breaks. **To speed registration, provide your business card along with your registration fee. You can also pre-register on-line through our pay-pal account.**

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

If you have colleagues who cannot attend the Symposium, please forward this program to them and let know they can mail their membership dues ($50) to our Treasurer, Victor Johnston (mailing address shown at left). Checks should be made out to SWCS.

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

**PARKING:** The best place to park is in garage marked on the map (last page), 4400 University.

We hope you enjoy the symposium!

Dan Shantz
Tulane University
Chair
2015 PROGRAM

All talks & breaks will be held in Melcher Hall, Room 150

7:30 AM  Registration – Victor Johnston, Treasurer (& helpers)

8:25 AM  Welcoming Remarks – Dan Shantz, Chair

8:30 AM  Bob Weber, Pacific Northwest National Lab “Heterogeneous Catalysis in Complex, Condensed Reaction Media”


10:00 AM  Coffee Break

10:30 AM  William Schneider, Notre Dame, “NOx Catalysis from the Bottom Up”


12:00 PM  Lunch Break and poster session – lunch is being provided!

1:30 PM  Southwest Catalysis Society Excellence in Applied Catalysis Award

Mike Wong, Rice University

1:45 PM  Mark Bussell, Western Washington University, “Nanoscale nickel phosphide catalysts for hydrodenitrogenation and hydrodesulfurization: In situ preparation at low temperature”

2:30 PM  Ye Xu, Louisiana State University, “Role of Oxygen Vacancy in the Surface Reactivity of CeO2(111)”

3:15 PM  Poster Awards and SWCS Business Meeting

In Melcher Hall, Room 150

3:30 PM  Adjourn
Heterogeneous Catalysis in Complex, Condensed Reaction Media

Robert S. Weber
Pacific Northwest National Laboratory, Institute for Integrated Catalysis

Many of the reactions required to upgrade biomass into fuels and chemicals—hydrogenation, hydrodeoxygenation, hydrocracking—are ostensibly similar to those practiced in the upgrading of petroleum into fuels. But, repurposing hydroprocessing catalysts from refinery operations has proved to be unsatisfactory. New catalysts are needed because the composition of the biogenic reactants differs from that of petroleum-derived feedstocks (e.g. the low concentration of sulfur in cellulose-derived biomass precludes use of metal sulfide catalysts unless sulfur is added to the reaction stream). New processes are needed because bio-oils oligomerize rapidly, forming intractable coke and “gunk”, at temperatures so low that the desired upgrading reactions are impractically slow, and so low that the bio-oil upgrading must be handled as a condensed fluid. Ideally, the new catalysts and processes would exploit the properties of the multiple phases present in condensed bio-oil, notably the polarizability and structure of the fluid near a catalyst’s surface.

This presentation will introduce a new type of support effect, for which there is evidence from homogeneous catalysis, and will discuss ways to implement and measure the hypothesized support effect and steer surface-catalyzed reactions to promote novel reaction mechanisms and to decrease catalyst deactivation.

Electrochemical Oxygen Reduction: Kinetic Analysis and the Development of Ag- and Pt-alloy Catalysts for Low Temperature Fuel Cells

Suljo Linic (ACS Catalysis Lecture)
Professor and 1938 Faculty Scholar
Director, Energy Systems Engineering Program
Department of Chemical Engineering
University of Michigan

The oxygen reduction reaction (ORR) is the major source of overpotential loss in low-temperature fuel cells. Expensive, Pt-based materials have been found to be the most effective catalysts, but exploration of alternatives has been hampered by stability constraints at the typical operating conditions of low pH and high potential.

I will discuss our studies of elementary mechanism of ORR on various metal electrodes using kinetic and micro-kinetic analysis of reaction pathways and quantum chemical calculations. These studies allowed us to identify the elementary steps and molecular descriptors that govern the rate of ORR. Using these performance descriptors we have been able to identify families of Pt and Ag-based alloys that exhibit superior ORR performance is acid and base respectively.

We have synthesized these alloys to demonstrate the superior ORR activity with rotating disk electrode experiments. We have also performed thorough structural characterization of the bulk and surface properties with a combination of cyclic voltammetry, x-ray diffraction, and electron microscopy with spatially resolved energy-dispersive x-ray spectroscopy and electron energy loss spectroscopy.
NO$_x$ Catalysis from the Bottom Up

**William F. Schneider**  
Professor of Chemical and Biomolecular Engineering  
Notre Dame University

In order to meet the increasing demands of energy sustainability and environmental protection, catalysis science and application in the 21st century has to be driven by basic insights into how catalytic materials function and how they can be improved. The advent of first-principles simulations based on density functional theory (DFT), which are able to reliably simulate chemical structures and reactions at the molecular scale, has been instrumental in the recent renaissance in heterogeneous catalysis research. In this talk, I will illustrate the capabilities and challenges of applying these simulation tools in the context of the catalytic chemistry of nitrogen oxides (NO$_x$). NO$_x$ is an unwanted by-product of combustion and is particularly difficult to remove from lean combustion sources, such as diesel engines. NO$_x$ also has rather complex chemistry that presents special challenges to simulation. I will describe some of our successes in understanding NO$_x$ chemistry from first-principles, with a first emphasis on recent work to capture the essential features of the beguilingly simple catalytic oxidation of NO to NO$_2$ over metals and metal oxides, to reconcile these models with experimental results, and to use these insights to guide the selection of new and improved catalysts. I will then discuss recent work to extend the same concepts to the selective catalytic reduction of NO$_x$ over narrow-pore metal-exchanged zeolites, a new class of effective and stable catalysts.

Design of Catalysts and Electrocatalysts for Energy Applications

**Jingguang G. Chen (ACS Olah Award winner)**  
Thayer Lindsley Professor of Chemical Engineering  
Columbia University

In the current talk we will use two examples to demonstrate the importance of using fundamental studies to identify and design catalysts and electrocatalysts. Our research approaches involve parallel efforts in density functional theory (DFT) calculations, surface science experiments on model systems, and synthesis and evaluation of supported catalysts under thermochemical or electrochemical conditions. We will first use water electrolysis to demonstrate the feasibility of using one atomic layer (monolayer) Pt on transition metal carbides (TMC) to achieve the same activity as bulk Pt. We will present DFT calculations of similar electronic and chemical properties between monolayer Pt/TMC and Pt, synthesis and characterization of monolayer Pt/TMC films, and electrochemical evaluation of the activity and stability of Pt/TMC for water electrolysis. Compared to the state-of-the-art Pt electrocatalyst, monolayer Pt/TMC catalysts represent a significant reduction in Pt loading for water electrolysis.

We will then use the conversion of biomass-derived oxygenates as an example to illustrate the advantages of bimetallic catalysts, which often show unique activity and selectivity over the corresponding parent metals due to the electronic modification and strain effect. We will present our results on the characterization of Ni/Pt bimetallic model surfaces and supported catalysts under in-situ reaction conditions, further highlighting the importance of using the combined approaches of DFT calculations, surface science experiments, and reactor evaluation for catalyst discovery.
Nanoscale Nickel Phosphide Catalysts for Hydrodenitrogenation and Hydrodesulfurization: In situ Preparation at Low Temperature

Mark E. Bussell
Professor
Department of Chemistry and Advanced Materials Science and Engineering Center
Western Washington University

Transition metal phosphides show excellent promise for hydrotreating reactions and the most active phosphides (e.g. Ni₂P/SiO₂) have exhibited higher hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activities than commercial sulfided Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts. However, the conventional synthesis of metal phosphate catalysts, which involves temperature-programmed reduction (TPR) of phosphate-based precursors, requires temperatures as high as 1100 K to produce the active phase. In addition, the strong interaction of phosphate with Al-containing supports complicates reduction of metal phosphate precursors on alumina (Al₂O₃), amorphous silica-alumina (ASA, SiO₂-Al₂O₃) and zeolites, and often results in poor performing catalysts relative to silica-supported metal phosphides. High reduction temperatures and the lack of versatility for supports make the use of metal phosphate catalysts less desirable for industrial hydrotreating applications. In this study, a novel synthesis method is described for the preparation of Ni₂P on SiO₂, Al₂O₃ and ASA from nickel hypophosphite precursors at 573-673 K. The results of a detailed investigation of the synthesis using TPR with on-line mass spectrometry (TPR-MS) will be presented. The in situ prepared Ni₂P catalysts exhibit high activities for the HDN of carbazole and HDS of benzothiophene, with the Ni₂P/Al₂O₃ and Ni₂P/ASA catalysts over three and two times more active, respectively, than similar catalysts prepared from nickel phosphate precursors.

Role of Oxygen Vacancy in the Surface Reactivity of CeO₂(111)

Ye Xu
Assistant Professor of Chemical Engineering
Louisiana State University

Ceria is an abundant and widely used technological material owing to its ability to readily store and release oxygen and change oxidation state. There is a growing body of studies indicating that ceria exhibits significantly different catalytic reactivity, including redox and C-C coupling reactions, toward a given organic molecule depending on the extent of reduction and crystalline orientation of the surface. This suggests that ceria is a promising candidate for the development of heterogeneous catalysts for the conversion of organic compounds, if its reactivity can be understood and tailored at the atomic level. In this talk I will discuss the roles of oxygen vacancy in the activation of simple organic oxygenates including acetaldehyde, formic acid, and acetic acid on the CeO₂(111) surface. Proposed reaction pathways and surface reaction intermediates are explored and calculated using density functional theory, followed by microkinetic modeling and simulation of infrared spectra. The results are compared with available
surface science experiments performed under controlled conditions, to elucidate the fundamental mechanisms through which these molecules interact with CeO₂(111).

**POSTER ABSTRACTS**

1. **Study of Cobalt Copper nanoparticle as catalysts for ethanol synthesis from syngas**  
   Zi Wang, James Spivey  
   Cain Department of Chemical Engineering, Louisiana State University, 110 Chemical Engineering, South Stadium Rd, Baton Rouge, LA 70803. Email: jjspivey@lsu.edu  
   This study uses microemulsion method to synthesize Cobalt and Copper composite catalysts for syngas to ethanol reaction. The effective site pairs for this mechanism are Cobalt and Copper metal with intimate contact. The catalyst is characterized by H₂ Temperature programmed reduction to study its reduction behavior. X-ray photoelectron spectroscopy is tested to determine the oxide phases of cobalt and copper composite. Transmission Electron Microscopy is used to observe the structure of the catalyst. The catalyst is reduced at 400 °C in H₂/He flow for three hours before reaction. After reduction, the reactor is pressurized to 40 bar and the temperature increases to 270 °C. Syngas with certain H₂ to CO ratio (H₂:CO=2:1) flows inside the reactor and catalytically converts to ethanol and other side products. The conversion is kept below 1% and the product is analyzed by a Shimadzu GC-2014 Gas chromatograph. The result reveals that the interactions between copper and cobalt are enhanced. Therefore more effective sites for ethanol formation are synthesized, which yields to higher ethanol selectivity than other bulk catalysts.

2. **The Effects of Surface Hydroxyl and Oxygen Species on the Partial Oxidation of Allylic Alcohols on Au(111)**  
   Gregory M. Mullen,¹ Liang Zhang,² Edward J. Evans Jr.,² Ting Yan,² Graeme Henkelman,² and C. Buddie Mullins¹,²,*  
   McKetta Department of Chemical Engineering¹ and Department of Chemistry,² Center for Nano and Molecular Science and Technology, Texas Materials Institute, and Center for Electrochemistry, University of Texas at Austin, Austin, Texas 78712-0231, United States. Email: gregory.m.mullen@gmail.com  
   In this study, we explored the partial oxidation of allylic alcohols on the Au(111) surface precovered with atomic oxygen and hydroxyl species via temperature programmed desorption and density functional theory methods. We found that these processes can occur via multiple pathways, dictated by the relative composition of surface intermediate species. All pathways proceed through alkoxide intermediates. Dehydrogenation of the alkoxide is the rate-limiting step of the partial oxidation process. This step can be promoted by both oxygen atoms and hydroxyl species. Hydroxyl species promote this reaction with nearly 100% selectivity towards partial the partial oxidation product, whereas, oxygen atoms can promote both partial oxidation and combustion pathways.
A Brief History of the Southwest Catalysis Society

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

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

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

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

In addition, catalysis groups were springing up at several universities, including surface science by the late John Mike White at the University of Texas, Jack Lunsford's and Wayne Goodman's highly productive groups at Texas A&M, Richard Gonzales at Tulane, Jim Richardson at U of H, Kerry Dooley at LSU, Tom Leland and me at Rice, and groups at other universities in the 5-state area. What was lacking? There was no formal mechanism for these diverse groups to exchange information or get advice in the southwest. The time was ripe for an organization where catalysis could be openly discussed. Although much catalysis research is proprietary, enough was sufficiently open to create a stimulating environment for sharing mutual interests, many focusing on new ultra-high vacuum analytical equipment that was being rapidly developed.
The first thing we did was to organize an NSF-supported workshop at Rice which (not surprisingly) concluded that more funding was needed for research on catalysts for fuels, environmental protection (cat converters), chemicals, etc. At that time, demand was also great for new employees with catalysis training, but the supply was quite limited. This provided an occasion for the development of short courses to train industrial employees in heterogeneous catalysis. Several courses were started around the country. One of the most successful was started at Rice and has continued for more than 30 years through the University of Houston. It can be said, then, that SWCS was instrumental in starting these heterogeneous catalysis short courses.

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

In 1985, the Southwest Catalysis Society was again called on to host a five-day 9th North American Meeting (NAM-9) at Houston's Adam's Mark Hotel. This time, Jack Lunsford and Lynn Slaugh were General and Vice Chair; I was Technical Program Chair. Most recently, the SWCS members organized the spectacular North American Meeting at Houston's downtown Hilton Americas Hotel in 2007, attended by over 1000 delegates from all over the world, “Celebrating Catalysis Texas Style.” Kudos again to SWCS officers Kerry Dooley, Brendan Murray, Scott Mitchell, Michael Reynolds, Yun-Feng Chang, Michael Wong, and many, many others! All told, the SWCS has hosted 3 national events now: 1971 (NAM-2), 1985 (NAM-9) and 2007 (NAM-20).
1. **Parking garage**: 4400 University Drive, Houston, TX 77204
2. **Melcher Hall**: building #528  ★ Room 150: symposium site
3. **Engineering Building 1**: building #579 (posters and lunch)

- red line: walking path from parking garage to SWCS symposium site
- red dashed line: walking path from symposium site to poster/lunch site