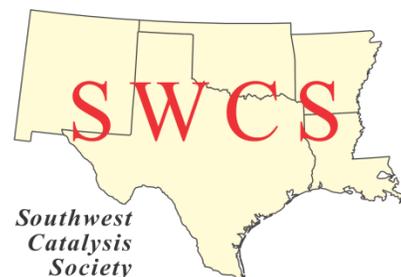


# SOUTHWEST CATALYSIS SOCIETY

## 2014 SPRING SYMPOSIUM



Friday, April 25, 2014

**\*Engineering Building 1 Room L2D2**

**University of Houston, Houston, TX**

Meeting sponsors:

# ExxonMobil



CRYSTAPHASE

HALDOR TOPSOE   
CATALYSING YOUR BUSINESS



SASOL  
reaching new frontiers





#### Chair

Bert Chandler  
Trinity University  
Department of Chemistry  
San Antonio, TX 78212  
bert.chandler@trinity.edu

#### Chair-Elect

Daniel Shantz  
SABIC Technology Center  
1600 Industrial Blvd  
Sugar Land, TX 77478  
dshantz@americas.sabic.com

#### Past-Chair

Andy Moreland  
Valero Energy Corporation  
San Antonio, TX  
andrew.moreland@valero.com

#### Secretary

Kerry Dooley  
Cain Chemical Engineering Dept.  
Louisiana State University  
Baton Rouge, LA 70803  
dooley@lsu.edu

#### Treasurer

Victor Johnston  
Celanese  
9502 Bayport Road  
Pasadena, TX 77057  
Victor.Johnston@Celanese.com

#### Directors

Jeff Rimer  
Department of Chemical &  
Biomolecular Engineering  
University of Houston  
Houston, TX 77204-4004  
jrimer@central.uh.edu

John W. Novak, Jr.  
Pacific Industrial Development  
Corp.  
18310 Old Trace Drive  
Baton Rouge, LA 70817  
jnovak@PIDC.com

Teng Xu  
ExxonMobil Chemical  
4500 Bayway Drive  
Baytown, Texas 77520  
teng.xu@exxonmobil.com

#### NACS Representative

Mike Reynolds  
Shell International Exploration and  
Production  
3333 Highway 6 South  
Houston, TX 77082  
mike.reynolds@shell.com

The SWCS officers and I welcome you to the 2014 SWCS Spring Symposium, **Friday, April 25, 2014**, at the University of Houston in the Engineering Building 1, Room L2D2 (building #580 on the University of Houston map on the back page).

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

The 2014 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 at \*XXXXXXXX

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. You will need a credit card to enter. We will have parking coupons available for drivers of cars to exit the garage for free. You will input the coupon upon exiting, then run your credit card, which will not be charged.

We hope you enjoy the symposium!

Bert Chandler  
Trinity University  
Chair

## 2014 PROGRAM

**All talks & breaks will be held in Engineering Building 1, Room L2D2**

- 7:30 AM** Registration – Victor Johnston, Treasurer (& helpers)
- 8:25 AM** Welcoming Remarks – Bert Chandler, Chair
- 8:30 AM** Steven Crossley, Department of Chemical Engineering, University of Oklahoma
- 9:15 AM** Pat Brant, Exxon Mobil
- 10:00 AM** Coffee Break and poster session
- 10:45 AM** Rob Rioux, Department of Chemical Engineering, Pennsylvania State University, “Single Molecule Investigations of Heterogeneous Catalysts: Probing Solvent Effects, Active Site Heterogeneity and [possibly] Adsorbate Dynamics”
- 11:30 AM** Christopher Jones, (Emmett Award Winner), Department of Chemical and Biomolecular Engineering, Georgia Institute of Technology, “Amine-Modified Silicates as Supports and Catalysts”
- 12:15 PM** **Southwest Catalysis Society Excellence in Applied Catalysis Award**  
Dr. Heiko Weiner, Celanese, for contributions to Celanese’s TCX® Ethanol Technology Commercialization
- 12:30 PM** **Lunch Break (in Engineering Building) and poster session**
- 1:45 PM** Paul Barger, UOP LLC, a Honeywell Company (F. G. Ciapetta Lectureship), Des Plaines, IL, “UOP Advanced MTO Technology – A New Route for the Production of Light Olefins”
- 2:30 PM** Charlie Campbell (Burwell Lectureship), Departments of Chemistry and Chemical Engineering, University of Washington “Supported Metal Nanoparticles: Correlating Structure with Catalytic Function via Metal Atom Energetics”
- 3:15 PM** Poster Awards and SWCS Business Meeting  
**In Engineering building**
- 3:30 PM** Adjourn

## Title

### Steven Crossley

Assistant Professor of Chemical and Biomolecular Engineering  
University of Oklahoma

abstract

## Title

### Pat Brant

Research Scientist  
Exxon Mobil Chemicals



## Single Molecule Investigations of Heterogeneous Catalysts: Probing Solvent Effects, Active Site Heterogeneity and [possibly] Adsorbate Dynamics

### Robert M. Rioux

Friedrich G. Helfferrich Assistant Professor of Chemical Engineering  
Pennsylvania State University



Metal nanoparticles are key components in the advancement of future energy technologies since they are catalytically active for several organic-inorganic syntheses, electron-transfer, and energy conversion reactions. They directly promote chemical conversion and/or facilitate chemical transport to active interfaces. A detailed understanding of the relation between structure and properties of nanoparticles will lead to tailored catalytic properties. Although these structure-function relationships are pursued by many researchers; they are typically limited to ensemble-level approaches where the intrinsic catalytic behavior of individuals is masked due to the asynchronicity of their behaviors during catalytic turnover. We employ a single molecule approach utilizing a two-state (pro-fluorescent to fluorescent) reduction reaction to examine the catalytic behavior of individual Au nanoparticles with single turnover resolution. Through kinetic modeling and isotopic labeling, we demonstrate competitive binding between solvent and substrate accounts for differences in observed catalytic rates at the ensemble level. Temperature-dependent measurements of the catalytic activity of single nanoparticles reveals heterogeneous in reactivity and kinetic parameters which are due to static dispersion even though the dispersion varies temporally; these variations are ascribed to the intrinsic reactivity of populations of indistinguishable active sites. Approaches to selectively titrate distinct active site populations on the surface of individual Au nanoparticles have enabled us to distinguish between their intrinsic kinetic behavior and utilizing ideal models of nanoparticle structures confirm their identity and concentration. The ability to probe reaction dynamics during single molecule catalysis studies utilizing an experimental and theoretical approach to understand delayed rise times in fluorescent response will be discussed.

## Amine-Modified Silicates as Supports and Catalysts

Christopher W. Jones (Emmett Award Winner)

New Vision Professor of Chemical and Biomolecular Engineering  
School of Chemical & Biomolecular Engineering  
Georgia Institute of Technology

Amine modified porous silicates are highly versatile materials. We have explored synthesis-structure-property relationships for these materials in the separation of organic species from gas or liquid phases, as well as for CO<sub>2</sub> capture. In this work, I will relate our recent endeavors in the design and application of porous silicate supported amines in catalysis. Both well-defined molecular amines and polymeric amines grafted to silicate surfaces will be described. Catalysts based on discrete molecular amines that act as basic sites and polymeric amines that cap and modify the reactivity of metal nanoparticles will be described in reactions of importance in synthetic organic chemistry.

---

**Southwest Catalysis Society Excellence in Applied Catalysis Award**  
**Heiko Weiner, Celanese Chemicals**

---

**UOP Advanced MTO Technology – A New Route for the Production of Light Olefins**

**Paul T. Barger (F. G. Ciapetta Lectureship)**  
Section Head – Catalyst Manufacturing Support  
UOP LLC, a Honeywell Company



The UOP Advanced Methanol-to-Olefins (MTO) Technology combines the UOP/Hydro MTO process for the conversion of methanol to light olefins with the Total Petrochemicals/UOP Olefin Cracking Process (OCP) to convert C<sub>4+</sub> by-products into additional ethylene and propylene. The overall process provides a cost-advantaged route for the utilization of natural gas, coal or biomass to produce these high volume petrochemicals. Fundamental understanding of catalyst structure-performance relationships and the MTO reaction mechanism have guided the development of this technology. The integration of the MTO and OCP processes provides close to 90% overall carbon selectivity to ethylene and propylene from methanol. Recent progress in the commercialization of this technology will also be reviewed.

**Supported Metal Nanoparticles: Correlating Structure with Catalytic Function via Metal Atom Energetics**

**Charles T. Campbell (Burwell Lectureship)**  
Rabinovitch Endowed Chair of Chemistry  
Departments of Chemistry and Chemical Engineering  
University of Washington



Many important catalysts for energy and environmental technologies involve late transition metal nanoparticles dispersed across the surface of some support material. The relationships between the energetic stability of late transition metal particles on oxide supports and their structural, electronic, chemisorption and catalytic properties will be examined. Oxide-supported metal catalysts have been studied using well-defined surfaces involving vapor-deposited

metals on single-crystal oxide surfaces, where the metal atoms nucleate and grow nanoparticles. The energetic stability of the metal atoms in these nanoparticles has been measured as a detailed function of particle size and support properties using metal atom adsorption calorimetry. The small-molecule chemisorption properties and sintering kinetics of these metal particles have also been measured. Trends in adsorption and metal / oxide adhesion energies will be reviewed. We find correlations amongst the energy of the metal atoms in these nanoparticles (i.e., their chemical potential, which depends both on their particle size their oxide support) and the strength with which they bond adsorbates, their catalytic kinetics and their sintering rates.

\*Johnson Matthey is gratefully acknowledged for sponsoring the Burwell Lectureship travel expenses

## POSTER ABSTRACTS

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

Daniel N. Tran and Kenneth J. Balkus Jr.

*University of Texas at Dallas – Department of Chemistry*

*800 W. Campbell Rd MS BE26*

*Richardson, TX 75080*

*\*[balkus@utdallas.edu](mailto:balkus@utdallas.edu)*

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

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

Tatyana V. Khamaturova, Dongmei Zhang, David E. Bergbreiter

*Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012*

*[tatyana.khamaturova@chem.tamu.edu](mailto:tatyana.khamaturova@chem.tamu.edu)*

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



## 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 C<sub>4</sub> 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.

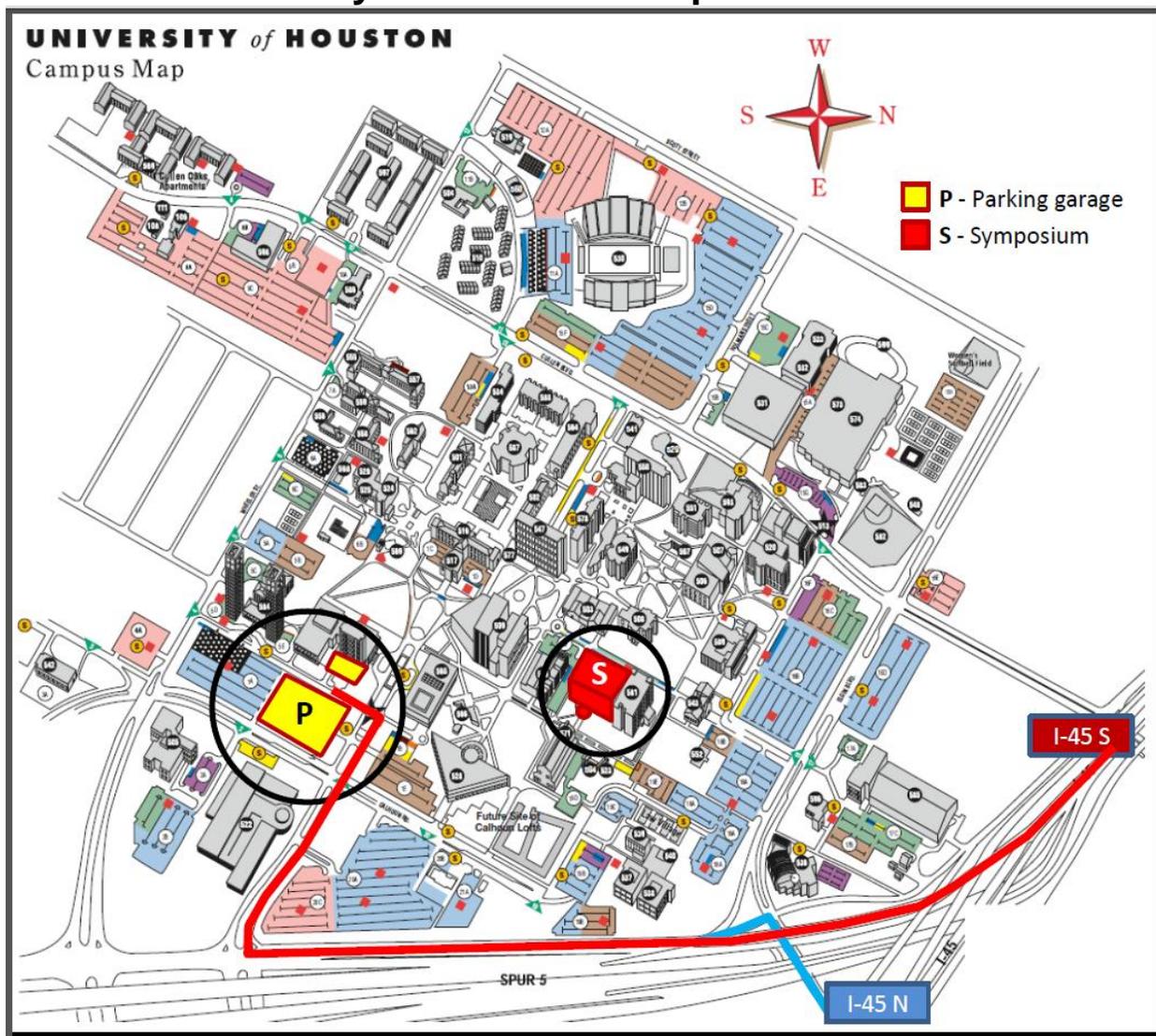


The first thing we did was to organize an NSF-supported workshop at Rice which (not surprisingly) concluded that more funding was needed for research on catalysts for fuels, environmental protection (cat converters), chemicals, etc. At that time, demand was also great for new employees with catalysis 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 Slauch 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).**

## University of Houston Campus information



### Directions: I-45 North

- Exit Elgin-Lockwood Cullen (44A)
- Turn Left on Elgin at the stoplight
- Go under overpass, turn left at stoplight onto TX-5 Spur S
- Turn right onto University Drive
- Continue on University Drive, cross Calhoun Rd.
- Welcome Center and **parking garage** are located on the left (Entrance 1)

**Address (Parking Garage):** 4400 University Drive, Houston, TX 77204

Alternative Parking: The Hilton Hotel across from the Welcome Center has a parking garage

**Address (Symposium):** 4800 Calhoun Rd., Engineering Building 1, Room L2D2 (#580 on campus map)

### Directions: I-45 South

- Take exit 44B toward State Route 5 S
- Merge onto TX-5 Spur S
- Turn right onto University Drive
- Continue on University Drive, cross Calhoun Rd.
- Welcome Center and **parking garage** are located on the left (Entrance 1)