

SOUTHWEST CATALYSIS SOCIETY

2016 SPRING SYMPOSIUM

Friday, April 22, 2016

Cullen College of Engineering Building 2, Room W122

University of Houston, Houston, TX

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The SWCS officers and I welcome you to the 2016 SWCS Spring Symposium, Friday, April 22, 2016, at the Cullen College of Engineering at the University of Houston in Engineering Building 2, Room W122.

We are delighted to present six invited speakers and 29 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 Commons area of the Cullen College of Engineering building 1.

Here is a link for registration, <http://www.eventbrite.com/e/southwest-catalysis-society-2016-spring-symposium-tickets-22584730537>. As always, pre-registration helps the SWCS committee to better organize the event. So we encourage you to pre-register via the link above. The registration fee is \$60 for regular members, and **\$20 for students and Post-doctoral individuals**, which includes North American Catalysis Society and SWCS annual membership dues, lunch, and coffee/snack breaks. For onsite registration, we can only accept either cash or checks – no credit cards. Please make your check payable to Southwest Catalysis Society (SWCS).

If you have colleagues who cannot attend the Symposium, please forward this program to them and let know they can mail their membership dues (\$60) to our Treasurer, Travis Conant (mailing address shown at left).

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

We have an exciting program for you, and look forward to seeing you at the symposium.

Teng Xu

Chair, SWCS
Global Chemical Research
ExxonMobil Chemical

2016 PROGRAM

All talks & coffee breaks will be held in Engineering Bldg. 2, Room W122

Lunch and the poster session will be held in Engineering Bldg. 1, Commons area

7:30 AM Registration & Breakfast – Travis Conant, Treasurer (& helpers)

8:30 AM Welcoming Remarks – Teng Xu, Chair

8:40 AM Johannes A. Lercher, Technische Universität München & Institute for Integrated Catalysis, Pacific Northwest National Laboratory, “Enhancing catalytic rates by constraints – the importance of the environment”

9:20 AM David G Barton, The Dow Chemical Company, “Serendipitous Discovery of a Nano-structured Yttrium Oxychloride Catalyst for the Selective Dehydration of Phenol”

10:00 AM Coffee Break

10:30 AM Xinhe Bao, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, “New Horizon of C1 Chemistry”

11:10 AM Scott Stevenson, SABIC Technology Center, Houston, “Paraffin Aromatization over Germanium-containing Zeolite Catalysts”

11:50 AM Lunch Break and poster session (Engineering Building 1 – Commons area)

**2:00 PM Southwest Catalysis Society Excellence in Applied Catalysis Award
Kerry M. Dooley**

2:10 PM Kerry M. Dooley, Louisiana State University, “Gasifier Effluent Conditioning / Cleanup – Catalysis and Adsorption”

2:50 PM Yuriy Román-Leshkov, Department of Chemical Engineering, MIT, “Architecture at the nanoscale: Engineering next-generation catalysts for energy applications”

**3:30 PM Poster Awards
Engineering Bldg. 2, room W122**

3:45 PM Adjourn

SPEAKERS (In the order of presentation)

Enhancing catalytic rates by constraints – the importance of the environment

Johannes A. Lercher

Department of Chemistry, Technische Universität München
Institute for Integrated Catalysis, Pacific Northwest National Laboratory



Understanding the elementary steps in acid-base and metal catalyzed organic transformations is a key for sustainable chemical conversions. Solid acids and bases with nano-pores such as zeolites act as solid Brønsted and Lewis acids, widely used as catalysts with well-defined acid-base sites and a well-defined reaction space around the sites. Within the pores of molecular sieves reacting molecules are constrained in a reaction space, which can be subtly adjusted via direct synthesis, as well as via the addition of cations, oxidic clusters or organic fragments. The impact of such changes on mono- and bimolecular reactions such as elimination reactions of alcohols, cracking and alkylation of hydrocarbons are discussed for gas and liquid phase reactions. Experimental methods to define the state of the reacting molecules combined with detailed kinetic analysis and theory will be used to explain the principal contributions of the interactions and the confinement to determine reaction rates. It will be discussed how reaction rates and pathways can be tailored using the space available for a transition state and the chemical constituents around the active site.

Biography

Johannes A. Lercher, studied Chemistry at TU Wien, receiving his PhD in 1981 at the same institution. After a visiting lectureship at Yale University, he joined TU Wien as Lecturer, later Associate Professor. 1993 he was appointed Professor in the Department of Chemical Technology at the University Twente, the Netherlands and in 1998 in the Department of Chemistry of TU München, Germany. Since 2011 he is also Director of the Institute for Integrated Catalysis at the Pacific Northwest National Laboratory, USA. He is external member of the Austrian Academy of Sciences as well as Member of the Academia Europaea and the European Academy of Sciences and Honorary Professor at several institutions in China. Author of over 500 papers and 19 patents, he is currently President of the European Federation of Catalysis Societies and Editor-in-Chief of the Journal of Catalysis. Recent awards include the Kozo Tanabe Award for Acid-Base Catalysis, the Burwell Lectureship of the North American Catalysis Society and the Francois Gault Lectureship of the Federation of European Catalysis Societies. His interests are related to catalysis in zeolites as well as on nanostructured oxides and sulfides, focusing on bifunctional and concerted catalysis, as well as understanding the influence of the steric and chemical environment on the properties of active centers in a catalytic site. .

Serendipitous Discovery of a Nano-structured Yttrium Oxychloride Catalyst for the Selective Dehydration of Phenol

Dr. David G Barton

The Dow Chemical Company



The use of solar technology has grown tremendously in recent years as the need for renewable energy sources increases. Concentrating solar power (CSP) represents a proven large-scale technology that uses parabolic trough technology, where solar energy is captured using mirrors that direct sunlight toward a collector containing a heat-transfer fluid (HTF). The equivalent of approximately 2 million homes is powered by CSP plants, corresponding to a savings of 2.5 million metric tons of CO₂ emissions per year. However, the tremendous worldwide growth in CSP is threatened by a chronic shortage of the heat-transfer fluid used to capture the solar energy in CSP plants. The standard fluid utilized in essentially all parabolic trough CSP systems is the most thermally stable (up to 400°C) organic fluid available today and consists of a eutectic mixture of diphenyl oxide (DPO) and biphenyl. The only commercially viable route to produce CSP-grade DPO involves the gas-phase dehydration of phenol over a heterogeneous thorium oxide (thoria) catalyst. The thoria-catalyzed process was discovered over 100 years ago, yet remains state-of-the-art and represents by far the most efficient process developed to date. However, there are two major shortcomings that seriously hinder further global DPO capacity expansion: (1) the thoria catalyst is mildly radioactive and poses significant health and environmental risks; (2) purified thoria sources have been unavailable globally in recent years.

Recently, in an effort to develop a more sustainable process by inventing new catalysts to produce DPO, the research team in Core R&D at Dow Chemical made a serendipitous discovery of a novel nano-structured yttrium oxychloride catalyst with unprecedented activity. This seminal discovery led to a new class of rare-earth catalysts for high-temperature dehydration reactions. This presentation will describe the discovery, characterization of the unique structure, and modeling efforts to describe the mechanism of these reactions.

Biography

David Barton is a Principal Research Scientist in the Inorganic Materials & Heterogeneous Catalysis Capability of Core R&D. In this role, David is responsible for technical project leadership, developing and shaping new projects, and subject matter expert for commercial catalysts/processes.

David joined Dow in 1998 in the Heterogeneous Catalysis organization. His work has focused on discovery of novel heterogeneous catalysts for the utilization of alternative feedstocks and environmentally benign processes including propylene epoxidation, methane activation, higher alcohol synthesis, propane dehydrogenation, phenol dehydration, and carbonylation reactions. He is the recognized technical expert in fundamentals of catalyst synthesis, in-situ characterization, mechanistic studies, reactor design for catalyst evaluation, and catalyst scale-up.

He is also a leader of external joint research collaborations with universities: UC-Berkeley, Univ of Minnesota, Northwestern Univ, and Georgia Tech; National Labs: National Renewable Energy Lab and Argonne National Lab; and catalyst vendors: Clariant and Evonik. He has given invited lectures at universities (Univ of Wisc, Ohio State, Univ of Kansas, and Stevens Inst), the Gordon Research Conference for Catalysis (2012, 2016), and national/international conferences (Heraeus Lecture, ACS, AIChE and NACS).

David graduated Summa Cum Laude in 1993 with his B.S. Chemical Engineering degree from the University of Minnesota and his PhD Chemical Engineering degree in 1998 from the University of California Berkeley working with Enrique Iglesia. He is the author of 18 US patents, 18 journal publications (>1800 citations), and >90 internal reports.

New Horizon for C1 Chemistry

Xinhe Bao

Dalian Institute of Chemical Physics, Chinese Academy of Sciences



Biography

Xinhe Bao received his PhD in Physical Chemistry from Fudan University in 1987 and then worked as a Fellow of Alexander von Humboldt in Fritz-Haber institute of Max-Planck Society in Berlin/Germany. He became a full Professor of the Dalian Institute of Chemical Physics (DICP, CAS) in China in 1995 and group leader of Nano & Interface Catalysis at the State Key Laboratory of Catalysis later. He held the position of the institute director from 2000 to 2007, and was appointed the President of Shenyang Branch of the Chinese Academy of Sciences in 2009. Bao is the member of Chinese Academy of Sciences, the member of the Academy of Sciences for the Developing World (TWAS) and the fellow of the Royal Society of Chemistry (UK). He is currently the vice President of Chemistry Society of China and the President of Chinese Society of Catalysis. Bao is Editor-in-chief of Journal of Energy Chemistry (JEC, Elsevier), and his name is listed in the editorial board or international advisory board of several international scientific journals, including Angew. Chem. Int. Ed., Energy & Env. Sci., Chem. Sci., Surf. Sci. Report, ChemCatChem, ChemPhysChem, Surf. Sci. and etc. His research focuses mainly on the fundamental understanding of catalysis, and its application to the development of new catalyst and catalytic process related to energy conversion, in particular clean coal and natural gas utilization. His achievements in catalysis of nanoporous materials, nano-structured carbon materials and nano-sized oxide particles, as well as in fundamental understanding of nano-confined catalysis have been well recognized worldwide. BAO has published more than 610 scientific papers and 1 book (Elsevier) with a citation over 14000 times, and filed 120 patents. He was awarded the prizes of National Science Award (second Class, 2005), Ho Leung Ho Lee Foundation for scientific and Technological Progress Award in Chemistry(2012), Award in Basic Science from Zhou Guang Zhao Foudation(2015) and Outstanding Science and Technology Achievement Prize of the Chinese Academy of Sciences(2015)

Paraffin Aromatization over Germanium-containing Zeolite Catalysts

Scott Stevenson, Alla Khanmamedova, Mike Huckman, and Dustin Farmer
SABIC Technology Center, Houston



While the conversion of naphthenes to aromatics is facile, C_6 to C_8 paraffins are more difficult to cyclize. We have developed a family of catalysts based on zeolites with framework germanium substitution that readily convert normal paraffins to the corresponding aromatics. In this talk, we will describe the constituents that comprise the catalyst and discuss what role each of them plays in achieving a selective conversion. We will also consider the reaction pathway, and discuss how, in a complex feed mixture, different components interconvert and (hopefully) end up as the desired products. Finally, we will discuss how the reaction network and kinetics determine how process conditions alter activity and selectivity.

Biography

Scott Stevenson received BA and BS degrees in Chemical Engineering from Oregon State University and a PhD in Chemical Engineering from the University of Wisconsin-Madison, where he worked with Professor Jim Dumesic on metal-support interactions and the synthesis and characterization of supported iron catalysts. After a post-doc in Physical Chemistry at the University of Munich with Professor Helmut Knözinger, Scott spent eight years at the Mobil Central Research labs in Princeton, New Jersey, where he worked on catalysts with environmental and refinery applications. Since joining SABIC's Houston lab in 1997, he has led teams in catalyst and new process development in a range of areas. He is currently a SABIC Research Fellow, a role in which he gives advice to many people, some of whom actually take it. He has co-authored 40 patents, 18 publications, and a book on strong metal-support interactions.

Southwest Catalysis Society Excellence in Applied Catalysis Award
Professor Kerry M. Dooley, Louisiana State University

Gasifier Effluent Conditioning / Cleanup – Catalysis and Adsorption

Kerry M. Dooley

Department of Chemical Engineering, Louisiana State University



It is estimated that more than 50% of the cost of producing syngas from biomass is in the cleanup / conditioning steps applied to the effluent (for coal, the percentage is higher). These steps include removal of S, N, Cl, alkali etc. and the reforming or cracking of “tar” compounds to CO, H₂, and lighter hydrocarbons. The tar reforming catalysis is closely related to other intensively researched processes such as CO₂ reforming or tri-reforming. In this talk progress in these areas will be reviewed, with special focus on our own work with rare earth oxide catalysts doped with transition metals, and similar materials used as high-temperature sulfur adsorbents. Transition metal-doped rare-earth oxides are more effective tar reformers than simpler mixed rare earth oxides or transition metals supported on (say) Al₂O₃, both in the absence and especially in the presence of sulfur. DFT calculations provide clues as to why this is so. Select catalysts have also been characterized by BET, TPR, TPO, XRD, XANES, EXAFS, Raman and magnetic susceptibility.

Biography

Kerry Dooley was educated at Tulane University (B.S., ChE), and, after a short stint as a process engineer for DuPont, at the Univ. of Delaware, where he completed his Ph.D. in superacid catalysis under the direction of Bruce Gates. Since that time he has been a Professor of Chemical Engineering (and adjunct in Chemistry) at Louisiana State Univ. His work is concentrated in catalysis / materials / reactor design, and he has published greater than 100 combined articles, patents, edited books and book chapters, and consulted for several companies. He currently holds the BASF Professorship, and was also a Fulbright fellow at the Univ. of Twente in the Netherlands.

Architecture at the nanoscale: Engineering next-generation catalysts for energy applications

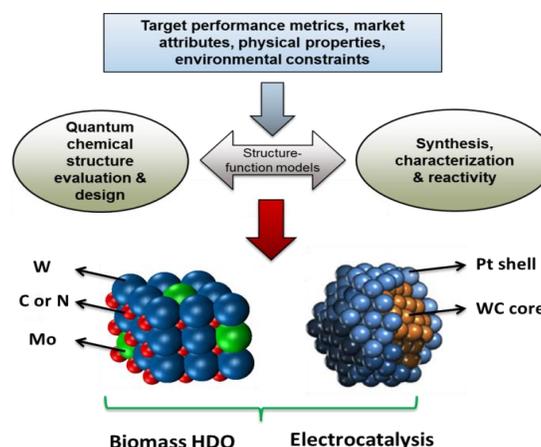
Yuriy Román-Leshkov

Department of Chemical Engineering, Massachusetts Institute of Technology



In an increasingly carbon-constrained world, lignocellulosic biomass, natural gas, water, and carbon dioxide have emerged as attractive options to supply energy, fuels, and chemicals at scale in a cleaner and more sustainable manner. However, the unique chemical makeup of these alternative energy sources has created daunting conversion challenges, requiring the development a new generation of robust, active, and selective catalysts.

In this lecture, I will show how advanced synthesis techniques can be coupled with rigorous reactivity and characterization studies to uncover unique synergies in nanostructured catalysts. Specifically, new developments in the use of heterometallic early transition metal carbide (TMC) nanoparticles will be described as a novel platform to replace (or at least drastically reduce) noble metal utilization in electro- and thermo-catalytic applications. A new method to synthesize TMCs and core-shell TMC-noble metal structures with exquisite control over composition, size, crystal phase, and purity will be demonstrated. The application of these materials will be presented in the context of selective hydrodeoxygenation of lignocellulosic biomass and for CO-tolerant electro-oxidation reactions.



Biography

Prof. Román was born in Mexico City, Mexico. He obtained his Bachelor of Science degree in Chemical Engineering at the University of Pennsylvania in 2002 and completed his Ph.D. at the University of Wisconsin-Madison, also in Chemical Engineering, under the guidance of Prof. James Dumesic. At UW he worked on developing catalytic strategies to convert biomass-derived carbohydrates into platform chemicals. Before joining the department of Chemical Engineering at MIT as an Assistant Professor, he completed a two-year postdoc at Caltech, working with Prof. Mark E. Davis on the synthesis of zeolites and mesoporous materials for the activation of small molecules and biomass-derived oxygenates. Prof. Román's has been awarded the SHPE Outstanding Young Investigator and the NSF CAREER awards.

POSTER ABSTRACTS

1. Oxidative Coupling of Methane: Impact of reactor type and catalyst composition

Aseem, Michael P. Harold*

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The oxidative coupling of methane (OCM) to higher molecular weight hydrocarbons has great appeal as an alternative route to chemicals and polymers. The reaction system is challenging because of large differences in the reactivity of the reactant methane and desired products (ethylene, ethane etc.) at the elevated temperatures (> 700°C) needed to activate methane. Moreover, the reaction system is highly exothermic and is noted for significant parametric sensitivity.

In spite of the large number of catalysts and reactor configurations have been studied over the past few decades, a catalyst and reactor combination has yet to be found out that gives sufficiently high C₂₊ yield to make this process commercially viable. The most studied catalysts to date for the OCM reaction system have been alkali-promoted alkaline earth metal oxides, transition metal oxides and rare earth metal oxides. Na₂WO₄-Mn/SiO₂ catalyst has attracted attention because of its comparatively favorable catalytic performance [1].

In this project first objective is to study different reactor types using the Na₂WO₄-Mn/SiO₂ catalyst. We have evaluated the fixed bed reactor and monolith reactor systems and obtained C₂₊ hydrocarbon yields between ~20% for the former to ~6% for later. The data shows that as the reaction system is oxygen limited beyond a particular temperature, the methane conversion is limited to ~32%. Thus distributed oxygen feed might be helpful to enable further reaction with the goal of achieving higher selectivity for desired products. Previous studies have shown favorable results through distributed oxygen addition [2]. In our current work we are using a porous asymmetric γ -alumina tubular membrane to contain the catalyst and provide distributed oxygen to a continuous stream of methane. By distributing the feed the aim is to maintain a low but uniform local concentration of oxygen along the catalyst bed length in order to avoid complete oxidation of desired products which in turn will increase the selectivity of C₂₊ hydrocarbons.

Another objective is to compare the OCM performance of multimetallic oxides prepared from alkali, alkaline and rare metal oxides with the much studied Na₂WO₄-Mn/SiO₂ catalyst. A comprehensive statistical analysis (analysis of variance, correlation analysis and decision tree) on database of OCM catalyst has reported that the high performance OCM catalyst should be multimetallic oxides based on one host metal oxide (La₂O₃ or MgO) with binary or ternary combinations. Alkali (Na, Cs) and alkaline earth metals (Ba, Sr, Mg) as dopants are reported to have positive effect on C₂₊ selectivity. The new catalyst combinations considered in this study are Cs-SrO/MgO, Cs-BaO/MgO and Cs-SrO/ La₂O₃.

References:

1. Arndt, S., Otremba, T., Simon, U., Yildiz, M., Schubert, H., Schomäcker, R, *Mn-Na₂WO₄/SiO₂ as catalyst for oxidative coupling of methane. What is really known?* (2012) Applied Catalysis A: General, 425-426, pp. 53-61
2. Lu Y., Dixon A.G., Moser W.R., Ma Y.H. ,*Oxidative coupling of methane in a modified γ -alumina membrane reactor* (2000) Chem. Eng. Sci., 55 (21), pp. 4901-4912

2. Co-oxidation of CO and Hydrocarbons on Pd/Ceria-Zirconia/Al₂O₃ Three-way Catalysts

Wendy Lang¹, Michael P. Harold¹, Yisun Cheng², Carolyn Hubbard², and Paul Laing²

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Three-way catalyst (TWC) light-off (LO) performance is critical in cost effectively meeting future automotive emission standards. Improvements in catalyst LO should include catalyst modifications and components that minimize inhibition effects of exhaust species, lowering precious group metal (PGM) loading, and using a lower cost PGM such as Pd. The light-off (ignition) and isothermal, steady-state behavior for individual oxidation and co-oxidation of CO and C₃H₆ under near-stoichiometric conditions was studied using fresh and aged Pd/Al₂O₃, Pd/Ceria-Zirconia (CZO), and Pd/CZO/Al₂O₃ monolith catalysts. CO and C₃H₆ were observed to be self- and mutually-inhibiting, with inhibition mitigated by the promotional effect of ceria-zirconia. Steady-state kinetics measurements using fresh Pd/Al₂O₃ and Pd/CZO/Al₂O₃ confirm negative reaction orders with respect to CO and C₃H₆.

3. Mechanistic Study of CO and Propylene Oxidation on Bimetallic Pt-Pd/Al₂O₃ Catalysts for Low Temperature Combustion Exhaust

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Stricter fuel economy standards have led the automotive industry to develop higher efficiency lean combustion modes. These modes need to meet environmental policies placed on the vehicle emissions before they are able to be commercially implemented. With the lower exhaust temperatures and higher CO and hydrocarbon concentrations, current catalytic exhaust systems may not be able to provide adequate activity. One of the key components due to the higher CO and hydrocarbon levels is the diesel oxidation catalyst (DOC). For this reason, we studied CO and propylene oxidation kinetics over bimetallic Pt-Pd/ γ -Al₂O₃ catalysts commonly used as oxidation catalysts in diesel exhaust systems. Powder catalysts containing Pt and Pd and various ratios thereof supported on Al₂O₃ were tested under simulated exhaust conditions on a bench scale reactor as well as using an in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) apparatus. From these experiments, surface intermediates observed in DRIFTS were related to observed light off behavior from bench scale reactor data for the different catalysts and some conclusions were drawn about the oxidation mechanisms of CO and propylene on the different Pt:Pd ratios. For instance, for CO oxidation, deactivation of Pd-rich catalysts by carbonates was observed, while CO poisoning by dicarbonyl species was observed on Pt-rich catalysts.

4. Impact of SO₂ on the NH₃-SCR reaction over Cu-SAPO-34: Ammonium sulfate versus other S-containing species

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Cu-CHA catalysts, such as Cu-SSZ-13 and Cu-SAPO-34, have been extensively used/studied as the NH₃-SCR catalysts for NO_x abatement applications. Compared to medium and large pore zeolites, Cu-CHA catalysts showed both higher hydrothermal stability and wider active temperature window. However, under operational conditions, these catalysts are prone to sulfur poisoning and hydrothermal aging¹⁻⁴. In the recent years, impact of sulfur on SCR performance over Cu-CHA has gained lot of attentions. These studies revealed that SO_x such as SO₂ and SO₃ severely inhibited low temperature (< 350 °C) SCR activity and oxidation functionality while high temperature SCR (> 350 °C) remained unaffected. They also revealed that sulfur poisoning in Cu-CHA catalyst has reversible nature and poisoned samples can be recovered by treating them at high temperatures (> 550 °C) and under lean condition. In terms of deactivation mechanism, it was reported that copper sulfate and ammonium sulfate are formed upon sulfur interaction with Cu-CHA catalysts^{1-3,5-7}. Despite of growing amount of studies, so many questions remained

unanswered on sulfur poisoning of SCR catalyst. For example, If ammonium sulfate is the primary low temperature SCR poison and decomposes at 300-350 °C, why are temperatures higher than 500 °C needed to recover low temperature SCR activity? Can we distinguish between the impact of ammonium sulfate and other sulfate species on NH₃-SCR? Then, what are the effects of non-ammonium sulfate S species on SCR performance? In this study, we evaluated the possible forms/states of S-containing species on Cu-SAPO-34 and the effect(s) of such species on SCR performance. Using transient experiments, we were able to distinguish sulfur poisoning caused by ammonium sulfate and other S-containing species. DRIFTS was used to study the effect of S-containing species on active Cu centers, and similarly the progression of the surface species during desulfation experiments. With these results, we evaluated the efficiency of a low temperature deSO_x protocol on SCR performance recovery.

References:

1. Cheng, Y. *et al.* The different impacts of SO₂ and SO₃ on Cu/zeolite SCR catalysts. *Catal. Today* **151**, 266–270 (2010).
2. Kumar, A. *et al.* Impact of different forms of feed sulfur on small-pore Cu-zeolite SCR catalyst. *Catal. Today* **231**, 75–82 (2014).
3. Zhang, L. *et al.* SO₂ poisoning impact on the NH₃-SCR reaction over a commercial Cu-SAPO-34 SCR catalyst. *Appl. Catal. B Environ.* **156-157**, 371–377 (2014).
4. Wang, D. *et al.* A comparison of hydrothermal aging effects on NH₃-SCR of NO_x over Cu-SSZ-13 and Cu-SAPO-34 catalysts. *Appl. Catal. B Environ.* **165**, 438–445 (2015).
5. Brookshear, D. W., Nam, J., Nguyen, K., Toops, T. J. & Binder, A. Impact of sulfation and desulfation on NO_x reduction using Cu-chabazite SCR catalysts. *Catal. Today* (2015). doi:10.1016/j.cattod.2015.04.029
6. Jangjou, Y. *et al.* Effect of SO₂ on NH₃ oxidation over a Cu-SAPO-34 SCR catalyst. *Catal. Sci. Technol.* (2016). doi:10.1039/C5CY02212F
7. Shen, M. *et al.* Deactivation mechanism of SO₂ on Cu-SAPO-34 NH₃-SCR catalysts: structure and active Cu²⁺. *Catal. Sci. Technol.* **5**, 1741–1749 (2015).

5. Experimental and kinetic modeling of lean-rich switching study over a modified TWC system

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With lean-burn combustion being more fuel efficient than more conventional stoichiometric combustion, its deployment is one strategy in meeting the upcoming CAFE standards for MYs 2017-2025 which require an average fuel economy exceeding 54.5 miles per gallon (MPG). Complicating its commercialization is the more stringent emission rules that will require an 80% reduction in non-methane organic gases (NMOG) plus NO_x from current Tier 2 Bin 5 levels. This poses a challenge for the elimination of NO_x (NO+NO₂) by traditional three way catalyst (TWC). An interesting technology to meet this challenge is the modified TWC catalyst with lean rich cycling. The upstream "TWNCS" comprises a TWC function with NO_x storage function, in order to accomplish NO_x storage/trapping during lean operation and modified TWC operation during stoichiometric operation. In this study a series of experiments was conducted on a commercial TWNSC monolith to understand the performance behavior under steady state and lean-rich cycling conditions. Steady state experiments were conducted with lean, rich and stoichiometric feeds over a wide range of feed temperatures, while the concentration of oxygen in the feed was varied to achieve a desired stoichiometric number. Lean-rich cycling experiments were also conducted to identify optimal conditions for achieving a specified conversion. A low-dimensional model of a catalytic monolith channel combined with modified TWC kinetic model was developed to capture the cycle activity and clarify the mechanism for regenerating reductants during periodic storage and regeneration. For the modified TWC kinetics study, a hybrid kinetic model including both elementary steps and overall reactions was used. The hybrid model accounts the kinetics of the oxidation of CO, H₂, NO and hydrocarbons, of the reduction of NO/NO₂ by CO, H₂ and representative hydrocarbons, and of the storage of NO_x and O₂. This study advances the understanding of modified TWC catalyst and provides guidance for optimizing catalyst formulation and operation strategies.

6. The Reductant Effects for Fast Lean-Rich Cycling Strategy of NO_x Reduction on Storage and Reduction Catalysts

Mengmeng Li, Yang Zheng, Dan Luss* and Michael P. Harold*

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Reductant effects of a fast lean-rich cycling strategy were investigated over a NO_x storage and reduction catalyst (NSR) containing Pt/Rh/BaO/CeO₂/Al₂O₃. As previous studies showed, the cycle-averaged NO_x conversion increases with frequency injection of propylene resulting in an expansion in the temperature range giving high NO_x conversion [1-3]. A systematic study was carried out to compare the effectiveness of individual reductants such as H₂, C₃H₆, C₃H₈ and their mixtures during both conventional NSR cycling (~ 1 min cycle time) and fast lean-rich cycling (~10 s cycle time) in a bench-scale reactor system. In contrast to C₃H₆, which is known to enhance NO_x conversion during fast injection operation, C₃H₈ is less effective during higher frequency cycling in the feed temperature range 250~325°C. The performance difference between the propene and propane is associated with the difference in their relative reactivities with oxygen and intermediates formation. In situ DRIFTS measurement shows the intermediates formation over LNT powder catalyst is different by using propene or propane, i.e. propene generated “C+H+O+N” to react selectively with NO to produce N₂, while propane requires dehydrogenation route first for intermediates generation.

References

1. Bisaiji, Y.; Yoshida, K.; Inoue, M. et al.; *SAE Int. J. Fuels Lubr.* 2012, **5**, 380.
2. Perng, C.C.Y.; Easterling, V.G.; Harold, M.P.; *Catal. Today* 2014, **231**, 125-134.
3. Zheng, Y.; Li, M.; Harold, M.; Luss, D.; *SAE Tech. Pap.* 2015, 2015-01-0984.

7. In situ Surface Studies of Zeolite Crystal Growth

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Zeolites are widely used in commercial processes spanning ion exchange to catalysis in the (petro)chemical industry. Understanding zeolite growth mechanisms at the molecular level is required for *a priori* selection of synthesis protocols that are capable of tailoring the physicochemical properties of zeolites. Despite tremendous effort, nucleation and growth pathways of zeolites are not well understood, due in large part to the inherent complexity of zeolite crystallization and the harsh synthesis conditions (i.e., high pH, high temperature etc.) that render *in situ* techniques challenging. Recently, our group developed a way to carry out solvothermal *in situ* atomic force microscopy (AFM) wherein we can observe zeolite surfaces at near molecular level under realistic growth conditions.[1]

Here, we will present *in situ* AFM measurements of silicalite-1 (MFI type) growth using zeolite growth modifiers (ZGMs) to modulate the shape of zeolite crystals. ZGMs are either molecules or macromolecules that selectively bind to zeolite crystal surfaces and mediate anisotropic growth to achieve desired crystal size and morphology. We have reported the efficacy of ZGMs in silicalite-1 synthesis.[2] Here, we will discuss the effect of ZGMs on silicalite-1 crystals using *in situ* AFM at realistic synthesis temperature (ca. 65°C). We observe differences in the relative rates of growth by two distinct pathways: classical processes involving molecule additional and nonclassical pathways involving the attachment of amorphous nanoparticle precursors. Silicalite-1 surface growth is monitored in the presence/absence of ZGMs. Moreover, we will present results of *in situ* AFM experiments with LTA crystals where we observe unique growth behavior at different supersaturation.



References:

1. Lupulescu, A.I. and J.D. Rimer, *In Situ Imaging of Silicalite-1 Surface Growth Reveals the Mechanism of Crystallization*. *Science*, 2014. **344**(6185): p. 729-732.
2. Lupulescu, A.I. and J.D. Rimer, *Tailoring Silicalite-1 Crystal Morphology with Molecular Modifiers*. *Angewandte Chemie-International Edition*, 2012. **51**(14): p. 3345-3349.

8. Identifying the Mechanism of SSZ-13 Crystallization and Methods to Tailor Material Properties

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Zeolite catalysts are used in a wide range of applications that span petrochemicals to biomass and natural gas conversion. Despite their extensive use in commercial processes, an understanding of their growth mechanism(s) remains elusive. The rational design of zeolite catalysts calls for more versatile synthetic approaches capable of tailoring crystal properties, such as crystal size, morphology, and composition. The ability to selectively tune these properties can improve catalyst performance (e.g., on-stream lifetime and conversion). Here, we will discuss the mechanism of zeolite growth involving transformations from amorphous precursors to the crystalline product.¹ To this end, we will focus on the industrially-relevant zeolite SSZ-13, which has a CHA type framework structure with 3-dimensional pores and small-pore aperture. We examined the temporal evolution of precursors and crystals at various stages of growth and observed a complex series of events involving precursor aggregation and structural rearrangements. As crystallization proceeds, there is a bimodal distribution of crystal size wherein smaller crystals are ~100 nm in dimension and larger crystals are of the order of 2 μm . The larger crystals exhibit rough surfaces and features with similar sizes as those in the small crystallites. We postulate that SSZ-13 growth involves crystallization by particle attachment (CPA) and that this process can be controlled through the judicious selection of growth modifiers.² We have successfully identified modifiers capable of tuning SSZ-13 crystal size by two orders of magnitude, ranging from 180 nm crystals (i.e., smallest size reported in literature) and large crystals (ca. 25 μm) that are amenable to AFM and diffusion studies. This facile method is unmatched in its ability to tune the physical properties of SSZ-13 crystals. Given the fact that modifiers are inexpensive and recoverable (post-synthesis), this practical approach to crystal engineering has the potential to be more broadly applicable to a wider range of zeolite framework types.

References:

1. De Yoreo, J.J., Gilbert, P.U.P.A., Sommerdijk, N.A.J.M., Penn, R.L., Whitelam, S., Joester, D., Zhang, H.Z., Rimer, J.D., Navrotsky, A., Banfield, J.F., Wallace, A.F., Michel, F.M., Meldrum, F.C., Cölfen, H. Dove, P.M.: "Crystallization by Particle Attachment in Synthetic, Biogenic, and Geologic Environments" *Science* 349 (2015), 6760-1/9
2. Kumar, M., Luo, H., Roman-Leshkov, Y., Rimer, J.D.: "SSZ-13 Crystallization by Particle Attachment and Deterministic Pathways to Crystal Size Control" *J. Am. Chem. Soc.* 137 (2015) 13007-13017

9. Comparison of One-dimensional Zeolites: Growth Pathways and the Effects of Crystal Modifiers

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Zeolites possess well-defined pores that provide desired shape selectivity for chemical reactions, which is one essential advantage of their use as catalysts in commercial applications. The geometry and dimensions of zeolite pores can influence diffusion, adsorption, and catalytic activity. One-dimensional (1D) zeolites, which impose

significant mass transfer limitations for internal diffusion, are promising catalysts for reactions such as methanol-to-hydrocarbons,^{1,2} isomerization, and cracking; however, large internal diffusion pathlength attributed to poorly engineered crystal size and habit often lead to rapid coking, which imposes restraints for commercial applications. When exploring methods to rationally design 1D zeolites with tailored physicochemical properties, we discovered that different 1D zeolite topologies share similar growth pathways that can be manipulated similarly by the adjustment of synthesis parameters (e.g., temperature and alkalinity). However, zeolites can have profoundly different interactions with organics used as either structure-directing agents (SDAs) or zeolite growth modifiers (ZGMs).³ To this end, we examined time-resolved pathways of crystal nucleation and growth, which predominantly involve nonclassical mechanisms associated with precursors (e.g., primary particles and/or bulk amorphous phases). These pathways can be altered through the judicious selection of synthesis parameters. Moreover, we have shown that ZGMs are an effective method to selectively alter the properties of zeolite crystals. The advantages of ZGMs are their versatility and low cost, which make them an attractive method of catalyst preparation. Our findings of 1D zeolite growth reveal general guidelines for improving mass transport properties, which has the potential to impact their performance in applications that span energy conversion to the production of value-added chemicals.⁴

References:

1. Wang, Q.; Cui, Z.-M.; Cao, C.-Y.; Song, W.-G. *Journal of Physical Chemistry C* **2011**, *115*, 24987.
2. Teketel, S.; Olsbye, U.; Lillerud, K.-P.; Beato, P.; Svelle, S. *Microporous and Mesoporous Materials* **2010**, *136*, 33.
3. Lupulescu, A. I.; Kumar, M.; Rimer, J. D. *Journal of the American Chemical Society* **2013**, *135*, 6608.
4. Teketel, S.; Skistad, W.; Benard, S.; Olsbye, U.; Lillerud, K. P.; Beato, P.; Svelle, S. *ACS Catalysis* **2012**, *2*, 26.

10. Effect of ZSM-11 Crystal Size on Methanol-to-Hydrocarbon Reactions

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ZSM-11 (MEL) is an emerging catalyst for a wide variety of applications. The MEL framework is very similar to MFI (i.e., ZSM-5), which is one of the most widely used zeolite catalysts in industry. Recent studies have shown that ZSM-11 has better catalytic performance in several different reactions compared to ZSM-5, possibly due to improved intra-crystalline diffusion within the straight channels of the MEL topology.¹⁻³ However, there are relatively few systematic studies of ZSM-11 synthesis, specifically with respect to tailored physicochemical properties such as size, shape, and composition (Si/Al ratio). Here, we present a systematic study of ZSM-11 catalyst preparation. Through the judicious selection of synthesis parameters, we successfully developed a facile protocol to generate a library of ZSM-11 catalysts with tunable size. More precise modification in ZSM-11 crystal morphology (or aspect ratio) can be accomplished through the use of zeolite growth modifiers (ZGMs), which are molecules or macromolecules that modulate the anisotropic growth rate of crystals with concomitant alterations in bulk habit.^{4,5} These methods for tailoring zeolite crystallization will be discussed along with catalytic tests using methanol-to-hydrocarbon (MTH) reactions. Collectively, these studies are part of a broader initiative to establish quantitative structure-performance relationships as a platform for optimizing zeolite catalysts.

References:

1. Kustova, M. Y.; Rasmussen, S. B.; Kustov, A. L.; Christensen, C. H., *Applied Catalysis B-Environmental* **2006**, *67* (1-2), 60-67.
2. Zhang, L.; Liu, H.; Li, X.; Xie, S.; Wang, Y.; Xin, W.; Liu, S.; Xu, L., *Fuel Processing Technology* **2010**, *91* (5), 449-455.
3. Bleken, F.; Skistad, W.; Barbera, K.; Kustova, M.; Bordiga, S.; Beato, P.; Lillerud, K. P.; Svelle, S.; Olsbye, U., *Physical Chemistry Chemical Physics* **2011**, *13* (7), 2539-2549.
4. Lupulescu, A. I.; Rimer, J. D., *Angewandte Chemie International Edition* **2012**, *51* (14), 3345-3349.
5. Lupulescu, A. I.; Kumar, M.; Rimer, J. D., *Journal of the American Chemical Society* **2013**, *135* (17), 6608-6617.

11. Effects of Zeolite Growth Modifiers on Different Stages of ZSM-5 Crystallization

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With the combination of excellent shape-selectivity, strong Brønsted acidity and high hydrothermal stability, zeolites are often used as heterogeneous catalysts in refinery and petrochemical processes. ZSM-5 is one of the most commonly used zeolites in industry. It has an MFI framework with 3-dimensional pores consisting of interconnecting straight and sinusoidal channels oriented along the [010] and [100] directions, respectively. Molecule diffusion is much faster in the straight channels, making these sites better suited for catalytic reactions. To this end, it is desirable to selectively control the [010] thickness of ZSM-5 crystals.

Here, we will present a novel approach to tailor ZSM-5 morphology that incorporates zeolite growth modifiers (ZGMs). The use of ZGMs has proven to be an efficient method to tailor the morphology of silicalite-1, which is the siliceous isostructural analogue of ZSM-5.¹ For our study of ZSM-5 synthesis in the presence of ZGMs, we assessed a library of modifiers previously screened for silicalite-1 to determine the influence of aluminum incorporation within the MFI framework. It was observed that subtle changes in the synthesis conditions can alter ZGM binding specificity to different crystallographic faces of ZSM-5. Using atomic force microscopy (AFM), we show that chemical force microscopy can probe modifier-crystal interactions in order to elucidate ZGM molecular recognition for different zeolite surfaces.²

Furthermore, we investigated the effects of ZGMs on the initial stages of amorphous precursor self-assembly and evolution (pre-nucleation) as well as crystal growth using a combination of two techniques: small angle X-ray scattering (SAXS)³ and dynamic light scattering (DLS). We observed that polycations have a unique effect of promoting precursor aggregation during the induction period. Collectively, this work provides quantitative guidelines for designing synthesis protocols to tailor ZSM-5 crystallization.

References:

1. Lupulescu, A. I.; Rimer, J. D. *Angew. Chemie - Int. Ed.* **2012**, *51* (14), 3345–3349.
2. Lupulescu, A. I.; Rimer, J. D. *Science*. **2014**, 729.
3. Fedekyo, J.; Rimer, J. D.; Lobo, R. et al. *J. Physical Chemistry C*. 2004, 108.

12. Catalytic Dehydrogenation of Methane using Transition Metals as Hydrogen Storage Materials

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Methane is the simplest hydrocarbon and is readily available. It constitutes 75% of natural gas, which has gained increased prominence in recent years due to the discoveries of new reservoirs. However, the direct conversion of methane into useful chemicals is limited due to the molecule's high symmetry and strong C-H bonds. In this work, we seek to upgrade methane to higher hydrocarbons. Presently, the most studied method for the upgrade of methane is the oxidative coupling of methane (OCM), $2\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O}$. In this reaction, the abstracted hydrogen reacts with oxygen to form water, which also provides the thermodynamic driving force to couple the methane into ethane. However, this method has failed to yield an economically viable process due to poor carbon selectivities, which are a result of the over-oxidation of the reactive CH_3 intermediate into CO and CO_2 . To avoid over-oxidation, we explore the use of hydride-forming metals to catalytically cleave the C-H bond, abstract the hydrogen, and form C_2 species in the absence of oxygen.

Through both DFT and experimental work, we have identified five Group III and IV metals (scandium, titanium, yttrium, zirconium, and hafnium) that have strong hydrogen storage capabilities and also exhibit the ability to perform the C-H bond scission. On the hcp(0001) surface of all five of the studied metals, we have found activation energy barriers under 1 eV for the reaction $\text{CH}_4 \rightarrow \text{CH}_3\cdot + \text{H}\cdot$, indicating the feasible activation of methane. The use of these hydridable metals and metal alloys is promising not only for the coupling of methane, but also for other methane upgrade reactions, such as HCN synthesis, and catalytic dehydrogenation reactions.

13. Catalyst Screening and Common Design principles for Hytrotreating: A DFT investigation on pure and promoted $\text{MoO}_3(010)$

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The high oxygen content (35-40 wt. %) of bio-oil produced from fast pyrolysis of biomass reduces its heating value and stability, and limits its subsequent use as a transportation fuel. Bio-oil may be upgraded via catalytic hydrodeoxygenation (HDO) and MoO_3 is a promising catalyst candidate for this reaction with high reactivity and selectivity.¹⁻³

Here, we used a realistic $\text{MoO}_3(010)$ facet obtained from an ab-initio thermodynamic phase diagram calculated under reaction conditions to investigate the HDO mechanism for furan, a common bio-oil model compound. Activation energy barriers for elementary reactions indicate that furan HDO on MoO_3 is facile, but similar to hydrodesulfurization (HDS), HDO requires the initial creation of a vacancy site where the feed molecule can adsorb. However, the oxygen vacancy formation on $\text{MoO}_3(010)$ is slow (high activation barrier) and highly endothermic. This scenario is reminiscent of HDS on MoS_2 ,⁴ where it is known that cobalt promotion facilitates sulfur vacancy formation, leading to increased activity of the industrially used CoMoS catalyst.

Using this existing knowledge of HDS on metal-sulfides as rational design guidelines, we investigated transition metal promotion (Mn, Fe, Co, Ni, Cu and Zn) on MoO_3 . From the phase diagram trends, it was found that transition metal promotion improves the ease of oxygen vacancy formation similar to HDS. These trends provide valuable insight for the determination of reactivity descriptors, which can be used to screen promoter materials for MoO_3 catalysts. The identification of reactivity trends and ability to rapidly screen promoters for MoO_3 will ultimately lead the way to rationally designing novel HDO catalysts for the commercial upgrade of biomass to chemicals and fuels.

References:

1. Prasomsri, T.; Nimmanwudipong, T.; Román-Leshkov, Y. *Energy Environ. Sci.* **2013**, 6 (6), 1732.
2. Prasomsri, T.; Shetty, M.; Murugappan, K.; Román-Leshkov, Y. *Energy Environ. Sci.* **2014**, 7 (8), 2660.
3. Shetty, M.; Murugappan, K.; Prasomsri, T.; Green, W. H.; Román-leshkov, Y. *J. Catal.* **2015**, 331, 86–97.
4. Moses, P. G.; Hinnemann, B.; Topsøe, H.; Nørskov, J. K. *J. Catal.* **2007**, 248 (2), 188–203.

14. Computational Catalysts Screening for CO, NO and Methane Oxidation at Reduced Temperature

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Diesel engine emissions, which typically include CO, hydrocarbons (HC), NO_x and particulate matter (PM), are a main contributor to environmental pollution. Recently, low temperature combustion (LTC) diesel engines have been developed, which have higher fuel efficiency and produce less NO_x and PM emissions compared to traditional diesel engines [1]. However, at the low exhaust temperature of LTC engines, CO and HC emission concentrations will increase. Meanwhile the activity of the commonly used diesel oxidation catalysts (DOC), Pt and Pd alloys, are reduced. All these factors lead to a major challenge for emission reduction and improved DOC catalysts with suitable activity at reduced temperatures are needed.

In this work, we apply a computational screening approach to search for promising DOC catalysts. To this end, we employ a micro-kinetic model for CO, NO and CH₄ oxidation reactions on transition metal alloys at reduced temperature diesel emission conditions to predict catalytic activity trends. Although CH₄ is not a main component of diesel engine emission, it is preliminarily chosen as the simplest hydrocarbon species. Existing energetic data for CO and CH₄ oxidations are adopted from literature [2,3]. NO oxidation data is obtained from density functional theory (DFT) simulations on 11 late transition metals. These energies are found to obey linear adsorption energy and transition state scaling relations. We are able to show empirically that only two variables – the binding energies of CO and oxygen – are needed as reactivity descriptors to predict all species' binding energies and reaction barriers. From this result we are able to construct the micro-kinetic model with only two descriptors, from which we can obtain volcano plots showing catalytic activity trends.

Based on our computational screening results, catalysts in the Ag and Au region are shown to have the good oxidation activity and oxidize CO, NO and methane simultaneously at 425 K. In contrast, if a catalyst in the Pt and Pd region is used, any produced NO₂ will immediately react with CO to generate NO and CO₂. The ability to simultaneously oxidize CO, NO and methane is beneficial for tuning the NO/NO₂ ratio for the downstream selective catalytic reduction (SCR) unit, which constitutes a big advantage for potential Ag and Au based catalysts. Our ongoing efforts aim towards our ultimate goal of predicting reliable oxidation activity trends for CO, NO and propene oxidation under low temperature DOC conditions.

References:

1. Musculus, M. P. B.; Miles, P. C.; Pickett, L. M. *Prog. Energy Combust. Sci.* **2013**, *39*, 246–283.
2. Jiang, T.; Mowbray, D. J.; Dobrin, S.; Falsig, H.; Hvolbæk, B.; Bligaard, T.; Nørskov, J. K. *J. Phys. Chem. C* **2009**, *113*, 10548–10553.
3. Wang, S.; Petzold, V.; Tripkovic, V.; Kleis, J.; Howalt, J. G.; Skúlason, E.; Fernández, E. M.; Hvolbæk, B.; Jones, G.; Toftelund, A.; Falsig, H.; Björketun, M.; Studt, F.; Abild-Pedersen, F.; Rossmeisl, J.; Nørskov, J. K.; Bligaard, T. *Phys. Chem. Chem. Phys.* **2011**, *13*, 20760–20765.

15. Methane Activation by Surface Oxygen Species on Au(111), Pd(111) and Au₃Pd(111): When an alloy is better than the sum of its components

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The use of methane, the main component of natural gas, as feedstock for the chemical industry is very appealing owing to its abundance and low cost.¹ In spite of these favorable facts, the potential for the production of value-added products from methane has not been fully realized. The primary challenge for methane utilization is the molecule's strong C–H bond and symmetric geometry without obvious point of attack.² Consequently, the rate-determining step for nearly all methane conversion reactions is the first C–H bond breaking step, or methane activation.³ Yet, Au-Pd/TiO₂ nanoparticles have been shown as effective catalysts for selective oxidation of methane to methanol using hydrogen peroxide as oxidant.⁴ The most likely active oxidants for the reaction are surface-bound OOH* and OH* species, which are derived from the surface decomposition of hydrogen peroxide. However, the participation of other surface oxygen species such as O* and O₂* can not be excluded. Inspired by Hutchings' work on Au-Pd alloy catalysts, we conducted a density functional theory (DFT) study to explore low

energy methane activation pathways in the presence and absence of surface oxygen species on Au₃Pd(111), Au(111) and Pd(111) model surfaces. We note that the Au₃Pd(111) alloy has isolated palladium surface atoms surrounded by gold atoms, and resembles the single atom alloy catalysts for which exceptional activity and selectivity has been reported.^{5,6} Our DFT results show that all of the oxygen species including O*, OH*, OOH*, and O₂* promote methane activation on Au(111), but inhibit the process on Pd(111). The bimetallic Au₃Pd(111) alloy merges the advantages of each of its single metal components in terms of thermodynamics and kinetics. Moreover, the over oxidation of methane on Au₃Pd(111) is less likely due to the selective formation of methyl bound to Au-sites, which are by themselves less reactive than Pd for C–H bond activation. Our results provide unique insight into the role of oxygen for C–H bond activation on Au₃Pd alloy and pave the road for the design of novel selective catalysts for the conversion of methane to value-added products.

References:

1. Lunsford, J. H.; *Catal. Today* 2000, **63**, 165-174.
2. Hammond, C.; Conrad, S.; Hermans, I.; *ChemSusChem* 2012, **5**, 1668-1686.
3. Trincherro, A.; Hellman, A.; Grönbeck, H.; *Surf. Sci.* 2013, **616**, 206-213.
4. Rahim, M. H. A.; Forde, M. M.; Jenkins, R. L.; Hammond, C.; He, Q.; Dimitratos, N.; Lopez-Sanchez, J. A.; Carley, A. F.; Taylor, S. H.; Willock, D. J. Murphy, D. M.; Kiely, C. J.; Hutchings, G. J.; *Angew. Chem. Int. Ed.* 2013, **52**, 1280-1284.
5. Kyriakou, G.; Boucher, M. B.; Jewell, A. D.; Lewis, E. A.; Lawton, T. J.; Baber, A. E.; Tierney, H. L.; Flytzani-Stephanopoulos, M.; Sykes, E. C. H.; *Science* 2012, **335**, 1209-1212.
6. Liang, S.; Hao, C.; Shi, Y.; *ChemCatChem* 2015, **7**, 2559-2567.

16. Simulated Temperature Programmed Desorption of Acetaldehyde on CeO₂(111): Evidence for the Role of Oxygen Vacancy and Hydrogen Transfer

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Typical biomass processing routes produce mixtures containing large fractions of small organic oxygenates including aldehydes, carboxylic acids, ketones and alcohols. However, their low molecular weights and high oxygen contents are undesirable in the production of fuels and higher value chemicals. Recently reducible oxides have been suggested as potential catalysts for the conversion of these organic oxygenates, via selective C-C coupling and deoxygenation reactions. We have studied the temperature programmed desorption (TPD) of acetaldehyde adsorbed on partially reduced CeO₂(111) in detail using microkinetic modeling based on self-consistent, periodic density functional theory calculations at the GGA+U-PW91 level. The outcomes of our microkinetic model are in close agreement with the observed desorption activities in TPD and infrared evidence for surface species. According to our proposed mechanism, oxygen vacancies play the critical role of activating the carbonyl bond by stabilizing the negatively charged O atom with exposed Ce⁴⁺, which facilitates the transfer of hydrogen atoms among the organic moieties and the formation of enolate that can lead to potential C-C coupling reactions. The reactivity difference between acetaldehyde and acetic acid on CeO₂(111) will also be compared and highlighted.

17. Insights into Nitrate Degradation over Indium-on-Palladium Model Catalysts

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Nitrate (NO_3^-) is one of the most ubiquitous groundwater contaminants, and is detrimental to human health, and arises due to the overuse of nitrogen-rich agriculture fertilizers, wastewater discharge and contaminant leaching from landfills. Nitrate, in addition to its partially reduced form, nitrite (NO_2^-), can cause adverse health effects in humans including methemoglobinemia and blue baby syndrome. Bimetallic PdIn catalysts have been found to be a promising solution to treat nitrate and nitrite contaminated water due to their high activity and selectivity to dinitrogen,¹⁻³ however, the mechanism of how the addition of the promoter affects the performance of the catalyst is unknown.

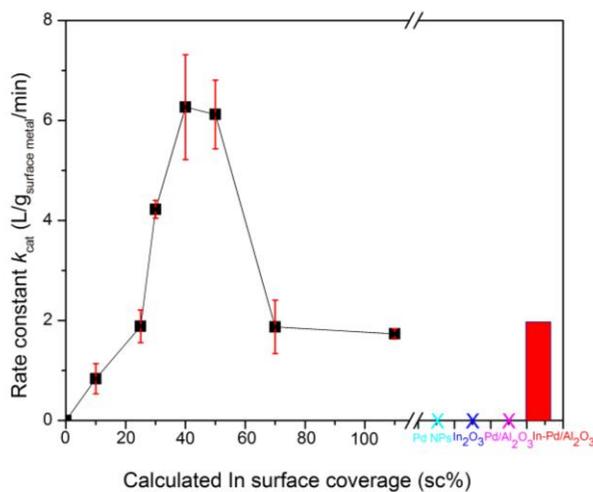


Figure 1. Experimentally determined nitrate reduction rate constants for In-on-Pd NPs as a function of In surface coverage and for monometallic Pd catalysts

To gain insights into the nitrate reduction mechanism, we reduced various amounts of In onto Pd nanoparticles (In-on-Pd NPs) corresponding to different surface coverages (sc%) and characterized them by TEM, XPS and in situ XAS. We found the In-on-Pd NPs show catalytic activity that varies with a volcano-shape dependence on In sc%. The NPs were maximally active at an In surface coverage of 40 sc%, with a pseudo-first order normalized rate constant of $k_{\text{cat}} = 6.27 \text{ L g}_{\text{surface metal}}^{-1} \text{ min}^{-1}$ and a calculated selectivity to N_2 of over 97%. Monometallic analogs (Pd NPs and In_2O_3 powder) showed no catalytic activity on reduction of nitrate (Figure 1). We hypothesize that the bimetallic InPd materials act as a bifunctional catalyst where the In is responsible for adsorbing and reducing nitrate, and Pd is responsible for regenerating these oxidized In atoms as well as for further reducing nitrite to dinitrogen or ammonia. These results were in agreement with the density functional theory (DFT) simulations, which found that adding In atoms reduce the energy barrier for nitrate binding. These results suggest that bimetallic In-on-Pd NPs have catalytic properties amenable for water NO_3^- remediation and may potentially be applicable to the treatment of other oxyanions such as perchlorate (ClO_4^-) and bromate (BrO_3^-).

References:

- Zhang, R.; Shuai, D.; Guy, K. a.; Shapley, J. R.; Strathmann, T. J.; Werth, C. J. *Elucidation of Nitrate Reduction Mechanisms on a Pd-In Bimetallic Catalyst using Isotope Labeled Nitrogen Species*. *ChemCatChem* **2013**(5) 313–321.
- Qian, H.; Zhao, Z.; Velazquez, J.; Pretzer, L. *Supporting palladium metal on gold nanoparticles improves its catalysis for nitrite reduction*. *Nanoscale* **2014**, 358–364.
- Gao, Z.; Zhang, Y.; Li, D.; Werth, C. J.; Zhang, Y.; Zhou, X. *Highly active Pd-In/mesoporous alumina catalyst for nitrate reduction*. *J. Hazard. Mater.* **2015**(286) 425–431.



18. Toward the In-situ Heterogeneous Catalyzed Degradation of 1,4-Dioxane in Water

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1,4-dioxane is an industrial solvent, contaminates up to 46% of personal care consumer products, and is a suspected carcinogen. It is also a stabilizer for chlorinated volatile organic compounds (CVOCs) with concentrations ~1-5 wt%, and is often present as a co-contaminant in CVOC groundwater plumes. Unlike CVOCs, however, 1,4-dioxane is infinitely soluble in water and has a very low Henry's law constant, making traditional remediation techniques such as carbon adsorption and air stripping ineffective. Bioremediation has potential, but degradation is slow and can be inhibited by the presence of CVOC co-contaminants. In situ chemical oxidation processes are also promising, but suffers from the need for an acidic environment and non-specific degradation which requires excessive oxidant.

We propose the use of solid metal oxide materials for the in situ selective degradation of 1,4-dioxane in groundwater by hydrogen peroxide. We screened several commercially available materials known to heterogeneously catalyze the decomposition of hydrogen peroxide for their activity in 1,4-dioxane degradation. Under batch conditions in the dark and at neutral pH, we found that the most effective catalysts - those with high and efficient 1,4-dioxane degradation - were not necessarily those with high hydrogen peroxide degradation activity. While the ability to decompose H₂O₂ is important, we propose that the best materials also have Lewis acid sites capable of binding 1,4-dioxane. Using a mixed metal oxide composed of zirconia (good H₂O₂ degradation activity) and tungsten oxide (high Lewis acidity), we found a catalyst capable of degrading 1,4-dioxane with a surface-normalized pseudo first order rate constant of 0.78 mL m⁻² h⁻¹ and a hydrogen peroxide usage efficiency of 1.22 mmol dioxane degraded per mole H₂O₂. We envision that the catalyst may be deployed using existing groundwater treatment technologies such as those used for permeable reactive barriers, where the catalyst is incorporated into the barrier and reactant is added upgradient from the barrier.

19. Indium on Palladium Nanocubes as Catalyst for Nitrate Reduction Reaction

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Nitrate contamination arises from agricultural fertilizers, sewage discharges and leachate from landfill, and can lead to serious human health problems such as cancer, thyroid function problems, and infantile methemoglobinemia (blue baby syndrome). Traditional methods to remove NO₃⁻ from water, such as ion exchange resins or reverse osmosis, generate a concentrated phase that still requires further treatment. The use of bimetallic InPd nanocatalysts to reduce NO₃⁻ in drinking water to dinitrogen has been proposed as a superior technology, but little is known about the catalytic mechanism.

The objective of this work is to study the effect of catalyst structure on nitrate reduction activity using In-on-Pd nanocubes (NCs). We first synthesized four different Pd NCs of mean diameters of 11.2 ± 1.80, 18.2 ± 2.51 and 23.5 ± 2.22 nm. In was then reduced onto the surface of the cubes, with calculated surface coverages ranging from

0-160 sc%. For the 11 nm NCs, the nitrate reduction reaction activity exhibited a volcano-shaped dependence on In loading, exhibiting a maximum activity of $\sim 110 \text{ L}_{\text{gsurface metal}}^{-1} \text{ min}^{-1}$ at 60 sc% and is $\sim 15\text{x}$ more active on a $\text{L}_{\text{gsurface metal}}$ basis than a catalyst made by depositing In on 3 nm Pd/Al₂O₃ catalyst. We attribute the increased activity to the relative higher proportion of Pd atoms in the (100) crystal face on the Pd NCs. In addition, the good selectivity to dinitrogen (>90%) over ammonia suggests In-on-Pd NCs are a promising catalyst to treat nitrate in groundwater.

20. Gold-MoS₂ Nanostructures for Plasmon- Driven Hot Electron Injection

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Plasmonic nanoparticles and quasi-2D (Q2D) transition metal dichalcogenides (TMDs) have been identified as promising materials for solar-to-fuel energy conversion. Q2D MoS₂ is known to be catalytically active for driving the hydrogen evolution reaction (HER). Adding plasmonically active materials to Q2D MoS₂ is a promising strategy to enhance photocatalytic activity further, because their large absorption cross-sections and non-radiative decay of plasmons into hot electrons can enhance both, light absorption and charge carrier generation, in adjacent Q2D MoS₂. Recent work on MoS₂ has investigated the electron-hole recombination mechanisms with optically excited carriers. Here, we synthesize hybrid Au/Q2D MoS₂ nanostructures in liquid suspension and characterize their ultrafast dynamics by femtosecond transient absorption (TA) measurements.

21. Engineering Transition Metal Dichalcogenides as Efficient Light Absorbers and Catalysts for Solar Energy Conversion

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Transition metal dichalcogenides (TMDs) have drawn much interest as two-dimensional (2D) materials due to their unique properties for solar fuel generation. In particular, monolayer molybdenum and tungsten dichalcogenides are shown to be catalytic active for water-splitting and CO₂ reduction in electrocatalysis based on experimental and theoretical studies. One of the challenging in using using these monolayer materials as solar energy conversion devices is the weak absorption of incident solar illumination. Here, we describe initial demonstrations and future prospects of three-dimensional photoelectrode architectures, which can largely increase absorption within the monolayer [1]. The improved light absorption is achieved by a planar cavity composed of a dielectric spacer and a reflector. Based on our previous studies, NiOx is an excellent candidate as a dielectric spacer layer. These photoelectrode architectures have been shown to achieve enhanced light absorption compared to MoS₂ monolayer alone, which should translate into an increased photocurrent for driving the water splitting reaction and CO₂ reduction.

‡ Photon management strategies for monolayer MoS₂, Shah Mohammad Bahauddin, Hossein Robotjazi and Isabell Thomann, submitted

22. Synthesis of Wrinkled Mesoporous titanosilicate for selective oxidation of cyclohexene

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Titanium containing molecular sieves have been widely studied as heterogeneous catalysts for selective oxidation using hydrogen peroxide or organic hydroperoxides. The superior epoxide selectivity of isolated framework Ti sites in olefin epoxidation has driven the effort to prepare different Ti molecular sieves. In particular, mesoporous Ti molecular sieves enable the oxidation of large organic substrates which cannot diffuse into the micropores of Ti-zeolites. We will report the synthesis of a series of Ti containing wrinkled mesoporous silicas (WMS) having a radial pore structure. Ti periodic mesoporous organosilicas (PMO) were also synthesized with the same radial pore structure. These catalysts were further modified by trimethylsilylation to improve the surface hydrophobicity. The unique radial wrinkled pore structure of these catalysts offers advantages over conventional Ti-MCM-41 having a one dimensional pore structure in the epoxidation of cyclohexene using t-butyl hydroperoxide. For oxidation of cyclohexene without solvent, silylated Ti wrinkled mesoporous silica shows a maximum turnover frequency of 1401 h⁻¹ with an epoxide selectivity of 95%.

23. Rare Earth / Transition Metal Oxides for Syngas Tar Reforming

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Syngas cleanup represents more than 50% of the total cost to produce ethanol from a biomass or coal gasifier. A major downstream problem is the deactivation of catalysts by sulfur and tars, both of which must be converted or removed to low ppm levels. Studies indicate that in tar reforming supported Ni catalysts show low sulfur tolerance except at high temperature (e.g., 1123 K).¹ Rare earth oxides (REOs) (e.g., Ce/LaOx) doped with transition metals (e.g., Mn, Fe) show promising results for tar reforming in the presence of sulfur.² In this study, highly amorphous, homogeneous mixed REO (e.g., Ce/LaOx) and REOs with base transition metal (e.g., Mn, Fe) catalysts were synthesized to perform both reforming and cracking of propane (model compound) in syngas effluents. Propane was chosen because it contains both C-C and C-H bonds, but is still simple enough for its adsorption and reaction to be modeled using the DFT + U method.³

The mixed oxide catalysts (numbers represent molar ratios) Fe/Ce₃, Pd/Ce₇, Ce₃/La, and Mn/Ce₄ give high and stable C₃ conversions with a low water (~10%) feed characteristic of the effluent from an air-blown gasifier. The catalysts Fe/Ce₃, Pd/Ce₇, and Mn_{0.2}/Ce/Zr show high and stable C₃ reforming activity when the water composition in the feed was increased (>20%) to be more characteristic of a steam-blown gasifier. The catalyst FeCe₃ shows the best C₃ reforming activity (on average) with both low and higher water feeds.

In parallel with this effort, DFT modeling was used to study both C-H and C-C bond activation on doped Ce(111) surfaces. Also, selected as-calcined and used catalysts were characterized by X-ray diffraction (XRD), X-ray absorption near edge structure (XANES), X-ray absorption fine structure (XAFS), temperature-programmed oxidation (TPO), temperature-programmed reduction (TPR), Raman spectroscopy, and magnetic susceptibility measurements. The characterizations showed that the catalysts remained (mostly) as doped REOs, without phase separation.

References:

4. Sato, K.; Shinoda, T.; Fujimoto, K. *Journal of Chemical Engineering of Japan* 2007, 40, 860.
5. Li, R., Roy, A., Bridges, J. and Dooley, K.M., *Ind. Eng. Chem. Res.* 2014, 53, 7999.
6. Krcha, M., Dooley, K. and Janik, M., *J. Catal.* 2015, 330, 167.

24. Boron-Carbon Composite Nanoparticles for the Enhancement of Biofuel Combustion

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Biofuels such as ethanol are good candidates to partially replace fossil fuels. However, the adoption of biofuels is inhibited by low energy densities and instances of incomplete combustion. Boron additives are a promising solution because they are among the most energy-dense materials. Boron can increase the overall heat release of the fuel and reduce its ignition temperature. A major challenge with boron is that it can be difficult to ignite, may not completely burn, and oxidizes relatively quickly in air. We synthesized boron nanoparticles with a carbon core-shell in order to address these issues: carbon ignites and burns at relatively low temperatures while the core-shell enables longer-term storage at ambient conditions.

B-C composites were synthesized by wet-chemical methods with the goal of producing elemental boron (zero valent) with a carbon core-shell. The composites were characterized by TGA/DSC, XRD, DRIFTS, SEM/EDX, and TEM. The combustion properties of the B-C composites with ethanol were determined by batch combustion in a calorimeter. The effects of the “shell” carbon on both ignition and fuel conversion were positive in almost all cases.

25. Enhanced Reaction Selectivity in Biphasic Systems using Responsive and Functionalized Silica Nanoparticles

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Silica in biphasic systems have recently gained attention as Pickering emulsion stabilizers in the areas of underground oil recovery and heterogeneous catalyst supports due to their ability to undergo functionalization and tune the surface chemistry [1-4]. While a great deal of literature exists for nanoparticle stabilized Pickering emulsions, very little is known about the fundamental behavior of silica nanoparticles at the oil-water interface during reactions. In this contribution, Pd nanoparticles are supported on spherical silica nanoparticles with varying degrees of hydrophobic functional groups. A combination of detailed emulsion characterization is coupled with phase specific chemical reactions to quantify both the location of functionalized silica nanoparticles at an oil/water interface, as well as the role of diffusion across the interface for enhanced reaction control. Finally, this information is used to create a responsive system where reaction selectivity is tuned by changing the particles wettability reversibly.

26. Direct carbon-carbon coupling of furanics with acetic acid over Brønsted zeolite

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Acetic acid and furanic derivatives together, form a major fraction of the compounds yielded from torrefaction or pyrolysis of biomass. These compounds promote undesirable side reactions and deactivate catalyst which is a major concern in upgrading bio-oil. Traditional strategy to eliminate these acids was by converting them to acetone via ketonization reaction, but loss of carbon in the form of is CO₂ is associated with it. Here we report direct acylation

of methylfuran with acetic acid as acylating agent over acidic zeolite. Reaction mechanism involving dehydration of acetic acid as rate determining step would be discussed using temperature programmed desorption technique, reaction kinetics and DFT calculations. Since the presence of water is inevitable in all the streams produced from biomass, the effect of water on reaction rate and catalyst stability for this reaction will be presented which is of practical importance. This study illustrates a new path of C-C coupling to produce higher value chemicals from biomass without any carbon loss.

27. Methane Oligomerization using solid superacid HBr-AlBr₃

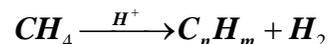
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With the advent of shale gas revolution, the production of natural gas has significantly increased. This has resulted in increased efforts to develop new technologies to convert natural gas into higher-value products. Activation of methane typically requires very high temperatures, e.g., indirect conversion of methane via syngas. Direct conversion, on the other hand, could greatly simplify the overall process. One direct conversion process involves the use of what is known as a “superacid”. A solid superacid catalyst has the necessary acidic strength to protonate methane and to subsequently break the C-H bonds, leading to higher carbon-number products. The overall reaction is:



Here, we present research focusing on the oligomerization of methane using a solid superacid catalyst (HBr-AlBr₃), based on earlier work in which this same catalyst was shown to convert ~99 % methane in the gas-phase [1]. Results from pyridine DRIFTS, and TGA experiments are presented to show characterization work on the synthesis of a series of solid catalysts that would be subsequently treated with HBr.

This work is supported by Chevron via the the Fund for Innovation in Engineering Research, supported directly to LSU.

References:

1. Vasireddy, S., S. Ganguly, J. Sauer, W. Cook, and J.J. Spivey, *Direct conversion of methane to higher hydrocarbons using AlBr₃-HBr superacid catalyst*. Chemical Communications, 2011. **47**(2): p. 785-787.

28. Synthesis and Characterization of the New Binucleating Tetrphosphine Ligand for Catalytic Applications

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Two new binucleating tetrphosphine ligands, *rac*- and *meso*-et,ph-P4-Ph (et,ph-P4-Ph = Et₂PC₆H₄(Ph)PCH₂P(Ph)C₆H₄PEt₂), have been synthesized, separated and fully characterized. A Grignard mediated P-C coupling reaction has allowed for a facile synthesis of the new tetrphosphine ligands. Both *rac*- and *meso*- forms of et,ph-P4-Ph have been characterized by NMR (¹H, ³¹P{¹H} and ¹³C{¹H}), high-resolution mass spectrometry and a number of Ni and Rh complex structures. The transition metal chemistry so far supports the far



stronger chelate effect in the ligands for coordinating metal centers. A variety of catalytic studies are underway using bimetallic complexes based on these new P4 ligands.

29. Is Palladium-Based Catalyst Beneficial for NO_x Abatement at Low Temperature?

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Selective catalytic reduction (SCR) of NO_x species is well-known for its effective conversion of said gases to N₂ but shows poor performance at low temperature or during the cold start of diesel engines. Therefore, the concept of *passive* NO_x adsorber has come along with an attempt to device a catalyst which can store NO_x at low temperature and release it at approximately 200°C where SCR performance becomes significant. Recent studies have shown promising NO_x storage capacity of various catalysts with metals supported on a wide range of materials, including metal oxides and zeolites. Among the reported metals, Pd stands out as the most favorable option, according to a patent by Johnson Matthey¹. However, few attempts have been made to understand why Pd-based catalysts have been reported to have remarkable NO_x abatement performance at low temperature. Therefore, this study will attempt to investigate the beneficial effects of Pd using Pd/ZSM-5 as a catalyst of choice. The NO_x storage performance of Pd/ZSM-5 was addressed by comparison to that of ZSM-5. The silica-to-alumina ratio of ZSM-5 was shown to also play an important role in NO_x storage.

¹ Rajaram, R.R.; Chen, H.-Y., and Liu, D. Passive NO_x Adsorber. U.S. Patent 20150158019 A1.



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

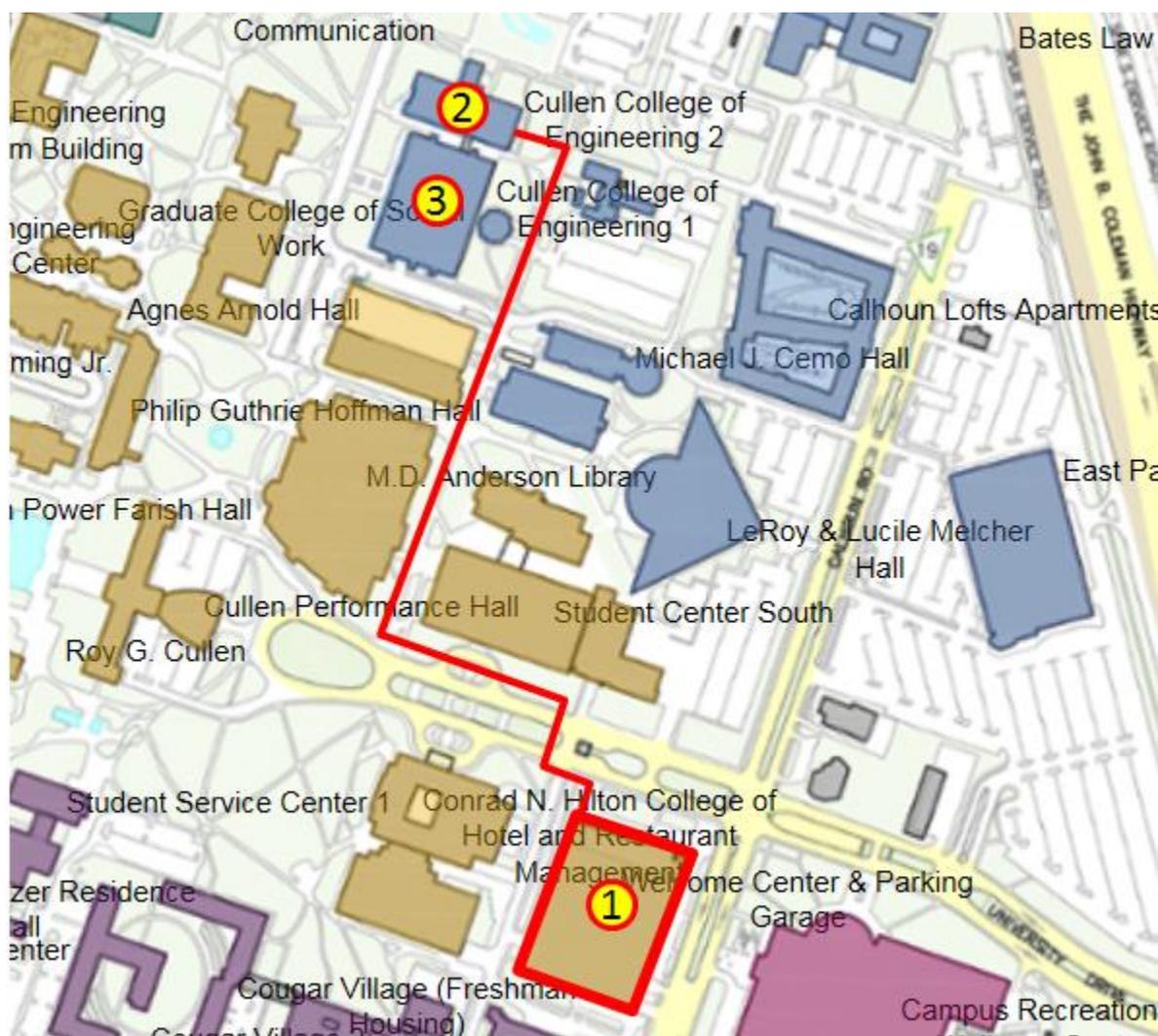


environment for sharing mutual interests, many focusing on new ultra-high vacuum analytical equipment that was being rapidly developed.

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 **Engineering 2:** Room W122 – Symposium site

③ **Engineering 1:** Commons area – Lunch and poster site

— Walking path from parking garage to SWCS symposium site