SOUTHWEST CATALYSIS SOCIETY

2017 SPRING SYMPOSIUM

Friday, April 28, 2017

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University of Houston, Houston, TX

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The SWCS officers and I welcome you to the 2017 SWCS Spring Symposium, Friday, April 28, 2017, at the Cullen College of Engineering at the University of Houston in the Houston Ballroom (Room 220 in the University Center).

We are delighted to present seven invited speakers and 40 poster presentations for this year's meeting. Meritorious posters presented by students and postdocs will be identified with **Best Poster Awards**, carrying cash prizes. The poster session will be held in the Houston Ballroom (Room 220, University Center).

The 2017 Spring Symposium **registration fee is $60**, which includes North American Catalysis Society and SWCS annual membership dues, lunch, and coffee/snack breaks. **Registration for students and post-doctoral individuals is $20.** To speed registration, provide your business card along with your registration fee. You can also pre-register on-line through our pay-pal account (http://swcatsoc.wixsite.com/swcatsoc/events).

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. Checks made payable to the Southwest Catalysis Society are accepted. 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 ($60) to our Treasurer, Travis Conant (mailing address shown at left).

The student registration fee is $20, which includes NACS and SWCS membership.

PARKING: The best place to park is in garage marked on the map (page 4), 4400 University Drive, Houston, TX 77204.

We hope you enjoy the symposium!

Jeffrey D. Rimer
University of Houston
Chair

2017 PROGRAM

All talks, coffee breaks, lunch, and the poster session will be held in the Houston Ballroom (University Student Center, Room 220)

7:15 AM **Registration – Travis Conant, Treasurer**

8:10 AM **Welcoming Remarks – Jeff Rimer, Chair**

8:15 AM **Joachim Sauer,** Humboldt University, Department of Chemistry
“Different C-H Bond Activation Mechanisms on Solid Oxide Catalysts”

9:00 AM **Ahmad Moini,** BASF Corporation
“Zeolite Catalysts for Diesel Emission Applications”

9:45 AM **Aditya Bhan,** University of Minnesota, Chemical Engineering & Materials Science,
“Chemistries Mediating Deactivation in Methanol-to-Hydrocarbons Conversion and Strategies to Mitigate Them”

10:30 AM **Coffee Break**

10:45 AM **Jeffery Bricker,** UOP Honeywell
“Recent Advances in Catalysis for Petrochemicals & Renewables”

11:30 AM **Alexis Bell,** University of California at Berkeley, Chemical & Molecular Engineering
“The Influence of Local Composition, Structure, and Confinement on Catalyst Activity and Selectivity”

12:15 PM **Lunch Break (Catered) and Poster Session in the Houston Ballroom**

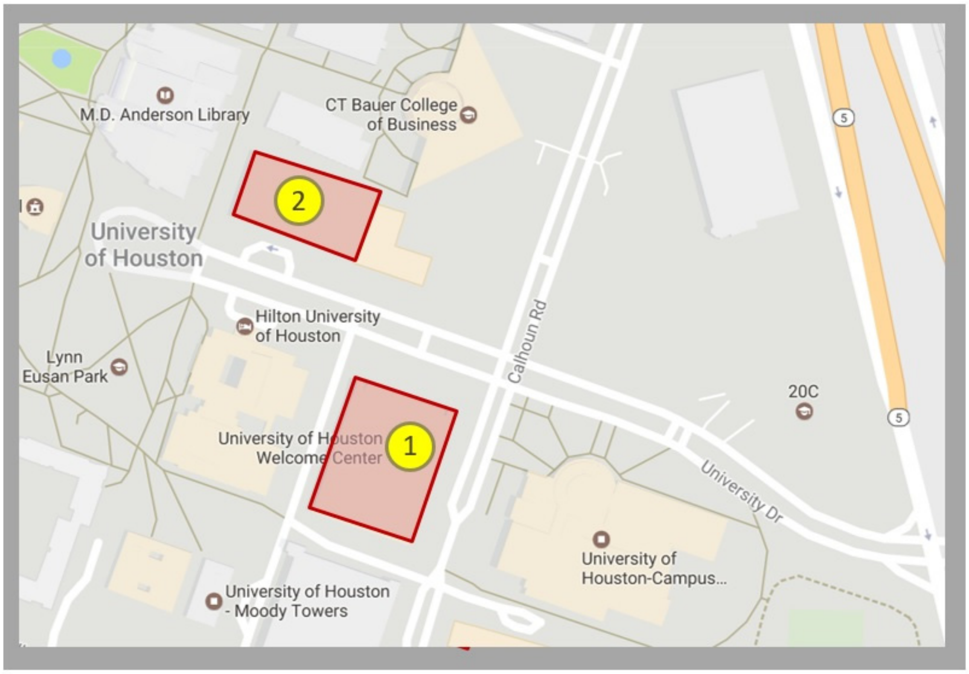
2:15 PM **Southwest Catalysis Society Excellence in Applied Catalysis Award**
Kathy M. Keville, ExxonMobil Chemical Company
Catalyst Development & Manufacturing

2:30 PM **Michael Wong,** Rice University, Department of Chemical Engineering
2015 Winner of the SWCS Excellence in Applied Catalysis Award
“Catalytic Nanoparticle Constructs for Clean Water Reactions”

3:15 PM **Giannis Mpourmpakis,** University of Pittsburgh, Chemical & Petroleum Engineering,
“Computational Design of Catalytic Nanoparticles”

4:00 PM **Poster Awards**

4:15 PM **Adjourn (Happy Hour at Pink’s Pizza, 4701 Calhoun Rd.)**



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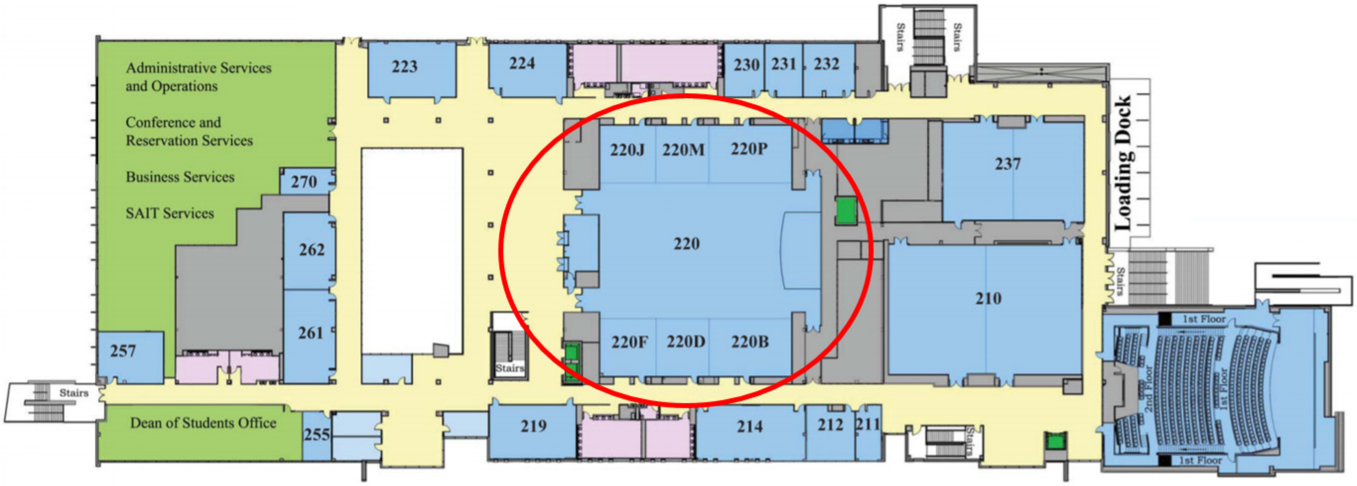
② **University Student Center:** Houston Ballroom, Room 220



University Drive (Main Entrance)

Different C-H Bond Activation Mechanisms on Solid Oxide Catalysts

Joachim Sauer
Humboldt University, Department of Chemistry

Two different types of catalytic C-H bond activations in partial oxidations are discussed: (i) activation by transition metal oxides which exchange redox equivalents with the feed molecule (Mars-van Krevelen), and (ii) activation on metal oxides where redox equivalents are exchanged directly between a hydrocarbon molecule and a surface oxygen species.

For the former, we are particularly interested in support effects for vanadium oxide catalysts, in particular in the difference between reducible (VO_x/CeO_2)[1] and non-reducible (VOx/SiO_2) supports.[2,3] For the latter, we discuss oxidative coupling of CH_4 on (Li-)doped and undoped MgO surfaces.[4]

1. T. Kropp, J. Paier and J. Sauer, *J. Am. Chem. Soc.,* 2014, 136, 14616.
2. J. Döbler, M. Pritzsche and J. Sauer, *J. Am. Chem. Soc.*, 2005, 127, 10861.
3. X. Rozanska, R. Fortrie and J. Sauer, *J. Am. Chem. Soc.*, 2014, 136, 7751.
4. K. Kwapien, J. Paier, J. Sauer, M. Geske, U. Zavyalova, R. Horn, P. Schwach, A. Trunschke and R. Schlögl, *Angew. Chem., Int. Ed.*, 2014, 53, 8774.

Biography

Joachim Sauer received the Dr. rer. nat. degree in Chemistry from Humboldt University in Berlin in 1974, and the Dr. sc. nat. degree from the Academy of Sciences in (East-)Berlin in 1985. Since 1993 he is Professor of Theoretical Chemistry at the Humboldt University in Berlin, and since 2006 external member of the Fritz Haber Institute (Max Planck Society). He is member of the Berlin-Brandenburg (formerly Prussian) Academy of Sciences, the German National Academy Leopoldina, and the Academia Europaea. His research has explored the application of quantum chemical methods in chemistry, with emphasis on surface science, particularly adsorption and catalysis. He has published more than 360 research papers, notably in the area of modeling the structure and reactivity of transition metal oxide catalysts and zeolites, and he has given more than 440 invited lectures. From 1999 to 2011 he was chairman of the Collaborative Research Center of the German Research Foundation (DFG) "Aggregates of transition metal oxides – Structure, dynamics, reactivity" and he is co-founder and principal investigator of the DFG-funded Cluster of Excellence “Unifying concepts in catalysis” in Berlin. He is one of the editors of the Journal of Catalysis.

Zeolite Catalysts for Diesel Emission Applications

Ahmad Moini
BASF Corporation

Automotive exhaust conditions present unique challenges for the design of effective catalysts. In addition to the need for catalytic activity over a wide temperature range, the catalyst must show durability towards extreme hydrothermal aging conditions. The use of zeolitic materials under such conditions is especially challenging due to the vulnerability of zeolites to steam aging. The BASF discovery of the Cu-CHA catalyst for selective catalytic reduction (SCR) of NO_x demonstrated an effective balance between favorable active sites and zeolite framework durability. It also paved the way for the implementation of urea SCR as the key approach for NOx reduction in diesel vehicles. This presentation will highlight the development of Cu-CHA as the leading technology for diesel emission applications. Specific focus will be placed on the synthesis and structural features of the zeolite. In addition, there will be a discussion of specific characterization and modeling approaches focusing on the unique attributes of the metal active sites and the interaction of these metal species with the zeolite framework.

Biography

Ahmad Moini is a Research Fellow at BASF Corporation in Iselin, NJ. He obtained his Ph.D. in Chemistry from Texas A&M University, and held a postdoctoral appointment at Michigan State University. Dr. Moini started his career at Mobil Research & Development Corporation (now ExxonMobil), where he conducted research on microporous materials. With a focus on exploratory zeolite synthesis, he studied the mechanism of zeolite crystallization and the role of specific classes of organic directing agents in the formation of various zeolite frameworks. He joined Engelhard Corporation (now BASF) in 1996. Since then, his primary research interests have been in the area of materials synthesis, directed at a range of catalytic and functional applications. He applied high throughput methods for the synthesis and evaluation of catalytic materials, and used these tools for the development of new products. A significant part of his work has been directed towards catalysts for environmental applications. These efforts, in collaboration with the extended BASF team, led to the discovery and development of Cu-CHA catalyst for selective catalytic reduction (SCR) of NOx from diesel vehicles. He holds 48 US patents relating to various aspects of materials and catalyst development.

Chemistries Mediating Deactivation in Methanol-to-Hydrocarbons Conversion and Strategies to Mitigate Them

Aditya Bhan
University of Minnesota, Department of Chemical Engineering & Materials Science

We demonstrate efficacy of a bifunctional strategy to improve the lifetime of CHA zeotypic materials (4x increase in turnover number) for the conversion of methanol-to-olefins (MTO) via physical addition of Y_2O_3 without disrupting the high selectivity to ethylene and propylene. We also reveal that the efficacy of this strategy increases with increasing proximity between the rare-earth metal oxide surface and acid sites inside the zeotypic material. This strategy is the result of our mechanistic inquiries about the identity and involvement of plausible intermediates and steps in MTH deactivation and the kinetic coupling made possible by the presence of acid and base catalytic functions within molecular diffusion distances. This strategy exploits:

(i) The scavenging of formaldehyde, derived in methanol dehydrogenation events, that reacts in Prins-type alkylation chemistries to transform active olefin- and aromatic- chain carriers in the dual-cycle 'hydrocarbon pool' mechanism that describes propagation events in MTO to unreactive polycyclic species;

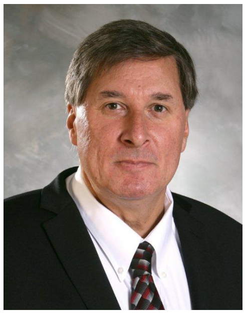
(ii) The previously unrecognized ability of Y_2O_3 and more generally of rare-earth oxides to selectively and catalytically decompose formaldehyde to CO_x in presence of unconverted methanol/DME reactants and methanol homologation products; and

(iii) The crucial role of formaldehyde transport between and within zeotypic domains in determining lifetime for MTO.

Biography

Aditya Bhan received his Bachelor of Technology (B. Tech.) in Chemical Engineering from IIT Kanpur in 2000 and his PhD in Chemical Engineering from Purdue University in 2005. From January 2005 to August 2007, he was a postdoctoral scholar at the University of California at Berkeley and since then he has been on the Chemical Engineering and Materials Science faculty at the University of Minnesota. Prof. Bhan leads a research group that focuses on mechanistic characterization of catalysts useful in energy conversion and petrochemical synthesis. His group at the University of Minnesota has been recognized with the Ipatieff Prize from the American Chemical Society, the DOE Early Career Award, the NSF Career Award, the 3M Non-tenured Faculty Award, and the McKnight Land Grant Professorship from the University of Minnesota.

Recent Advances in Catalysis for Petrochemicals & Renewables



Jeffery Bricker
UOP Honeywell

This presentation will discuss one of the most advanced new technologies for light olefin production. The landscape for industrial production of olefins is changing rapidly with intense commercialization of Methanol-to-Olefins (MTO) and on-purpose propane dehydrogenation technology, e.g. OleflexTM. The Oleflex dehydrogenation of propane to produce propylene has become a critical technology to fill the propylene shortage, which is increasing due to the portion of steam crackers now using inexpensive ethane feedstock [1]. This trend is expected to continue in the near future due to the abundance of wet shale gas worldwide [2]. As evidence, over ten million tons of on-purpose propane dehydrogenation capacity is expected in the next few years.

The development and commercialization of large scale light paraffin dehydrogenation technology required advances in both high temperature moving bed process engineering and catalysis [3-4]. The equilibrium limitations for dehydrogenation and impact on process design are discussed. Advanced dehydrogenation multi-metallic catalysts are prepared which < 1 nm and provide superior activity, selectivity, stability and regeneration, resulting in long life and superior process economics [5-6].

Today, renewable fuels technology has become a commercial reality with commercial jets and diesel vehicles employing fuels from renewable sources. These fuels have a significantly lower carbon dioxide footprint from life cycle analysis. We will discuss these recently commercialized catalytic technologies which convert biomass and triglyceride renewable feed sources into fuels.

1. K. Holmquist ,Oil and Gas Journal, 108, 27 (2010).
2. Petrochemicals, Chemical Week, March 27, 2011
3. US Patents 4,914,075; US 7,432,406; US 5,233,118; US 6,177,381
4. Vora, B.V., Topics in Catalysis 55, 1297-1308 (2012)
5. Advanced Catalytic Dehydrogenation Technologies for Production of Olefins, J.C Bricker and B.V. Vora Topics in Catalysis December 2012, Volume 55, Issue 19-20, pp 1309-1314
6. Carrazza, J., The 8th Middle East Refining and Petrochemicals Conference, Bahrain, May 20 (2012)

Biography

Jeffery Bricker is the Senior Director of Research at UOP, which provides expertise and conducts research in the areas of New Materials, Catalysis, Advanced Characterization & Analytical, Membranes, Bio-Renewables, and Exploratory Platforms. He received a Bachelor of Science in Mathematics and Chemistry from Heidelberg University in 1979 and a Ph.D. in Chemistry from The Ohio State University in 1983. He started at UOP as a catalyst scientist working in paraffin dehydrogenation, selective hydrogenations, natural gas utilization, and selective oxidation. Jeff has held a variety of positions in Refining, Petrochemical, and Separations R&D and has had a key role in development of several UOP technologies and products. In his current role, he is accountable for UOP's longer- range research programs and capabilities development. He has been awarded 61 U.S. patents and authored over 15 peer reviewed publications. He is a member of the North American Catalysis Society and the American Chemical Society. He frequently lectures on catalysis around the world. He has received a number of awards including the UOP Stine Star, the 2006 Honeywell Growth and Innovation Award, the 2008 Devon Meek Lecturer, the 2011 ACS National Award in Creative Invention, the 2015 Honeywell Distinguished Technologist Award, and the 2017 Eugene J. Houdry Award in Applied Catalysis by the North American Catalysis Society.

The Influence of Local Composition, Structure, and Confinement on Catalyst Activity and Selectivity

Alexis T. Bell
University of California at Berkeley, Department of Chemical & Biomolecular Engineering

The performance of catalysts is judged on the basis of their activity, selectivity, and stability. Remarkable progress in understanding how these properties are related to catalyst composition and structure at the atomic scale has come through the application of various forms of spectroscopy and more recently through the use of various forms of electron microscopy. Most recently, electronic structure calculations have added further information by validating the deductions drawn from experimental studies and providing answers to questions that cannot be addressed by experiments. The net result is that many, if not most, modern investigations of catalysis draw upon information from experiments and theory in order to develop a holistic understanding of catalyzed reactions. This talk will illustrate how this approach has been used to develop insights into the factors controlling the ammoxidation of propane to acrylonitrile over bismuth molybdate, the cracking and dehydrogenation of butane, and the electrochemical oxidation of water to oxygen. An important point to be drawn from these studies is that modern theoretical methods can provide answers not addressable solely by experiments, but to do so experimental observations are needed to help define the nature of active sites and their environment.

Biography

Alexis T. Bell received his BS and PhD degrees in chemical engineering from MIT and since 1967 has been a faculty member in the Department of Chemical and Biomolecular Engineering at the University of California, Berkeley, where he is now the Dow Professor of Sustainable Chemistry. His research is devoted toward developing a molecular-level understanding of how heterogeneous catalysts facilitate chemical reactions involved in the conversion of energy resources to fuels and the synthesis of chemicals with high selectivity. This effort combines a variety of experimental approaches. His research contributions have been recognized by numerous awards and lectureships, and by his elections to the National Academy of Engineering, the National Academy of Sciences, and the American Academy of Arts and Sciences. Prof. Bell has served as Chair of his department from 1981 to 1991, as Dean of the College of Chemistry from 1994-1999, and as interim Chair of his department from 2005 to 2006. He also serves the editor for Catalysis Reviews – Science and Engineering and as an editor of PNAS.

Catalytic Nanoparticle Constructs for Clean Water Reactions

Michael S. Wong
Rice University, Department of Chemical Engineering

By understanding the structure-property connection at increasingly fine detail, one can create materials to improve our understanding of chemical reactions at the molecular level, and to imbue them with enhanced catalytic performance (i.e., the three S's of speed, selectivity and stability). Through a synthesis-structure-property approach, there is tremendous potential for success in treating recalcitrant water-borne contaminants, for example, through catalytic hydrodechlorination (HDC). I will discuss our recent results on "catalytic denitrification," a process in which nitrate anions are chemically reduced to dinitrogen selectively using indium-decorated palladium (In-on-Pd) nanoparticles.

Biography

Michael S. Wong is Professor and Chair of the Department of Chemical and Biomolecular Engineering at Rice University. He is also Professor in the Department of Chemistry, Department of Civil and Environmental Engineering, and Department of Materials Science and NanoEngineering. He was educated and trained at Caltech, MIT, and UCSB before arriving at Rice in 2001. His research program broadly addresses chemical engineering problems using the tools of materials chemistry, with a particular interest in energy and environmental applications ("catalysis for clean water") and an emphasis on understanding synthesis-structure-property relationships in heterogeneous catalysis. Current research activities and interests are (i) structure-property analysis of palladium-on-gold catalysts; (ii) metal-on-metal nanoparticle synthesis; (iii) treatment of dioxane, nitrate, fluorocarbons, and chlorocarbons from water; (iv) sugar upgrading chemistry, and (v) nanoparticle assembly.

He has received numerous honors over the years, including the MIT TR35 Young Innovator Award, the American Institute of Chemical Engineers (AIChE) Nanoscale Science and Engineering Young Investigator Award, Smithsonian Magazine Young Innovator Award, Guest Professorship at Dalian Institute of Chemical Physics (DICP), and in 2015, the North American Catalysis Society/Southwest Catalysis Society (NACS/SWCS) Excellence in Applied Catalysis Award. He is Research Thrust Leader on 'Multifunctional Nanomaterials" and part of the Leadership Team in the NSF-funded NEWT (Nanotechnology Enabled Water Treatment) Engineering Research Center, based at Rice. He is Chair of the ACS Division of Catalysis Science and Technology (CATL), and serves on the Applied Catalysis B: Environmental editorial board. Previous service includes Chairmanship of the AIChE Nanoscale Science and Engineering Forum, SWCS Chairmanship, and Chemistry of Materials editorial board membership.

Computational Design of Catalytic Nanoparticles

Giannis Mpourmpakis
University of Pittsburgh, Department of Chemical & Petroleum Engineering

The physicochemical properties of metal nanoparticles, such as adsorption and catalytic behavior, as well as their stability, depend on the nanoparticle metal composition and morphological characteristics, such as size and shape. The high catalytic performance of metal nanoparticles is commonly a fine balance between their stability and activity. In this work we blend first-principles calculations with scientific computing to introduce a novel computational framework able to i) predict the stability of bimetallic nanoparticles of different morphology and metal composition ii) screen different bimetallic nanoparticles towards their adsorption performance and iii) design catalytically active and thermodynamically stable nanoparticles. Our methodology is applied to the capture (adsorption) and activation of CO2, a green-house gas, with the potential to be converted to fuels and chemicals.

Biography

Giannis (Yanni) Mpourmpakis is an Assistant Professor at the Department of Chemical and Petroleum Engineering at the University of Pittsburgh. His research focuses on the theoretical investigation of the physicochemical properties of nanomaterials, with applications in the nanotechnology and energy arenas. Prior to joining the University of Pittsburgh in 2013, he was a Senior Researcher at the Catalysis Center for Energy Innovation (CCEI), at the University of Delaware (2011-2013). Yanni graduated from the Chemistry Department, at the University of Crete, Greece (2001), where he also earned his MSc (2003) and PhD degrees (2006). His doctoral research focused on the theoretical design of novel nanomaterials for hydrogen storage applications. In 2006, he joined the Chemical Engineering Department at the University of Delaware as a postdoctoral researcher and investigated the catalytic behavior of metal nanoparticles and in 2008 he was awarded the “Marie-Curie” post-doctoral fellowship by the European Commission. He has published more than 60 research articles in high impact journals. His research has attracted significant awards, such as the CAREER award from the National Science Foundation in 2017, the Doctoral New Investigator award from the American Chemical Society (2016) and the “60th Nobel Laureate Meeting”, in which he was selected as one of the top 500 young researchers worldwide in 2010. For his contributions to education, Yanni was awarded the 2016 James Pommersheim Award for Excellence in Teaching in Chemical Engineering by the University of Pittsburgh.

2017 Southwest Catalysis Society Excellence in Applied Catalysis Award

Kathy M. Keville
ExxonMobil Chemical Company
Catalyst Development & Manufacturing

In recognition for original contributions to catalyst development and commercialization related to lube, refining, and petrochemical applications

Biography

Kathy M. Keville joined Mobil Research and Development Corporation's Paulsboro Research Laboratory in 1988. From 1988 to 1992 she worked in zeolite catalyst development with a focus on hydroprocessing and catalyst manufacture.

In 1992, Kathy moved to Mobil Chemical Company in Beaumont, Texas as the Catalyst Unit Engineer. From 1992 to 2000 she held various positions of increasing responsibility at the plant including engineering and business team leads. In 2000, Kathy moved to ExxonMobil Chemical Technology Licensing in Baytown, Texas. With ExxonMobil Chemical Technology Licensing she was a Catalyst Product Manager, Supply and Planning Manager, and Global Technology Manager. She assumed her current position of Catalyst Development and Manufacturing Support Manager in 2010.

Through Kathy's nearly 30-year career and over 50 patents, she has contributed in some aspect to every catalyst ExxonMobil has developed and commercialized, including dozens of different catalysts spanning refining, lubricant and chemical applications. These catalysts enable ExxonMobil and licensees to safely, efficiently and reliably produce clean fuels, high quality lubricants and important chemicals such as p-xylene, benzene, ethylbenzene and cumene.

Kathy graduated from Union College with a Bachelor of Science degree in Chemistry and from Purdue University with a Master of Science degree and a Doctor of Philosophy in Chemical Engineering. She has three children.

POSTER ABSTRACTS

1. Support Effects of Gold Nanoparticles for the Selective Hydrogenation of 1-Octyne

James Bruno, Alexander Huther, Nicolas Dwarica, William Moore, Stephen Thai, Christopher Pursell, and Bert Chandler*
Department of Chemistry, Trinity University, San Antonio, TX 78212
* bchandle@trinity.edu

Polyolefin feedstocks typically contain < 5% unsaturated impurities. These impurities, such as acetylene, 1-propyne, 1,3-butadiene, etc. poison downstream polymerization catalysts and must be removed to < 150 ppm. Nickel and palladium catalysts were traditionally used, but both have poor stability and selectivity. In this work, we studied support effects on gold nanoparticles for the selective hydrogenation of 1-octyne. Supports of varying reducibility and electron donor strength were evaluated in order to measure conversion and selectivity differences between catalysts. Even at low concentrations (150 ppm), the reaction was zero or negative order in 1-octyne. This suggests that the reaction is limited by hydrogen activation on Au and that the gold nanoparticles were poisoned by strongly-bound 1-octyne.

2. Anhydrosugar Synthesis through Acid-catalyzed Pyrolysis of Salt-Passivated Carbohydrate

Li Chen[a], Z. Conrad Zhang[c*], and Michael S. Wong[a,b,d,e*]
[a] *Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, USA*
[b] *Department of Chemistry, Rice University, Houston, TX 77005, USA*
[c] *Dalian National Laboratory of Clean Energy, Dalian Institute of Chemical Physics, Dalian, Liaoning 116023, China*
[d] *Department of Civil and Environmental Engineering, Rice University, Houston, TX 77005, USA*
[e] *Department of Materials Science and NanoEngineering, Rice University, Houston, TX 77005, USA*
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Selectively producing chemicals from biomass-derived carbohydrate pyrolysis is challenging in renewable chemical industry. Anhydrosugars are difficult to synthesis in large quantities due to various competing pathways in carbohydrate pyrolysis. Acid catalyst can enhance anhydrosugar's yield but it also activates other pathways. Here we demonstrate that an acid catalyst (e.g., H_2SO_4) together with an alkali salt (e.g., Na_2SO_4) improves anhydrosugar (such as levoglucosan, LGA) production from glucose pyrolysis. The addition of Na_2SO_4 enhance LGA yield by inhibiting ring opening, tandem dehydration and condensation reactions which were activated by the acid catalyst through salt-sugar complexation at the O1 position. Characterization data shows that salt will complex with sugar. The optical rotation data indicate that excess amount of sodium cations compete with H^+ for the oxygen site, therefore slow the glucose mutarotation reaction rate. Furthermore, sulfate anions can form the solvent cage to help stabilize the intermediate and assist the formation of LGA. The effect of cations and anions were further explored by pyrolyzing different alkali/alkaline earth metal salts. The salt and acid system can also be applied on more complex susbtrate.

3. Time-resolved *In situ* Surface Studies of Zeolite Crystal Growth

Madhuresh K. Choudhary[1], Manjesh Kumar[1] and Jeffrey D. Rimer[1*]
[1] *Department of Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204*
* jrimer@central.uh.edu

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

Here, we will present *in situ* AFM measurements of silicalite-1 (MFI) crystallization using zeolite growth modifiers (ZGMs) to modulate the shape of zeolite crystals. ZGMs are 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 synthesis temperatures of 60 – 75°C. We observe differences in the relative rates of growth by two distinct pathways: classical processes involving molecule addition and nonclassical pathways involving the attachment of amorphous nanoparticle precursors. Silicalite-1 surface growth is monitored in the presence/absence of ZGMs.

We will also present *in situ* AFM results of industrially relevant aluminum-containing zeolite LTA where we observe distinct growth regimes as a function of supersaturation. At high supersaturation, we observe the three-dimensional assembly and structural evolution of gel-like islands on LTA crystals leading to a mechanism of surface roughening that differs from kinetic roughening in classical theory. We also report a distinct switch in the growth mode at low supersaturation marked by two-dimensional nucleation of single layers with step heights corresponding to the composite building units of the crystal structure.

(1) Lupulescu, A. I.; Rimer, J. D.; *Science* 344 (**2014**) 729-732.
(2) Lupulescu, A. I.; Rimer, J. D.; *Angew. Chemie Int. Ed.* 51 (**2012**) 3345–3349.

4. Analysis of Light-Off during Oxidation of Reactant Mixtures on Pt/Al_2O_3 using Micro-Kinetic Models

*Rama Krishna Dadi, Dan Luss and Vemuri Balakotaiah**
Department of Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204
* bala@uh.edu

An elementary step mechanism, which accounts for adsorption, desorption and surface reaction steps is proposed for co-oxidation of CO, propylene, hydrogen and ethane on Pt/Al_2O_3. Parameter estimation is used to determine the kinetic parameters for these steps, which depend on platinum loading and dispersion. A micro-kinetic model is proposed for water-gas shift reaction that captures the experimental trend observed during co-oxidation of CO/H_2. This mechanism is used to predict hysteresis features during oxidation and co-oxidation reactions. The oxidation of all the individual reactants exhibits regular hysteresis and the model predicts the experimentally observed inverse hysteresis during co-oxidation of CO and C_3H_6. The inverse hysteresis is caused by surface intermediates formed during C_3H_6 oxidation. These surface intermediates (CH3 adsorbed species) block the active sites, decreasing the light-off activity of CO during ramp down. The developed micro-kinetic model can also explain steam reforming of propylene and ethane on Pt/Al_2O_3. Finally, we compare the predicted hysteresis during CO oxidation by global and micro-kinetic models. The predicted ignition temperature by both global and micro-kinetic models is almost same. However, the predicted extinction temperature by the global and micro-kinetic models is rather different. This behavior is due to different rate determining step during ramp down period.

5. The Study of Pt/γ-Al2O3 Aging and its Effect on Steady State Ammonia Oxidation

Pritpal S. Dhillon and Michael P. Harold*
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Stringent environmental rules and success of Selective Catalytic Reduction (SCR) technology has increased the importance of the Ammonia Slip Catalyst (ASC). The ASC is located downstream of the SCR and is intended to selectively convert un-reacted ammonia into nitrogen. Therefore, it makes SCR catalyst more flexible for dynamic driving conditions. To achieve high selectivity towards nitrogen, a dual layer ASC (top SCR and bottom PGM) is commonly used. However, the catalyst experience degradation under the severe operating conditions which affects the product distribution and conversion. Literature has suggested that hydrothermal aging degrades Cu/SSZ-13 (SCR) actives sites for (NH_3+NO) reaction [1], which may lead to the increase in NO selectivity of the dual layer ASC, adversely affecting nitrogen selectivity. To elucidate the effect of hydrothermal aging on the base PGM layer of the ASC, we performed a systematic aging study of steady state ammonia oxidation experiments on single layered Pt/γ-Al_2O_3. Our study explains the effect of aging on catalyst morphology and how its activity changes for ammonia oxidation reaction. Our results reveal that hydrothermal aging has negligible impact on Pt/Al_2O_3 activity at temperature below 250 °C but a significantly detrimental impact on activity at temperatures exceeding 300 °C. Based on our results, we a developed mathematical model to quantify the decline in catalyst activity with aging time for ammonia oxidation reaction. The characterization results and mathematical model predicts that the transport limitations and change in washcoat morphology are the likely underlying mechanism for the decline in activity of the catalyst.

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6. Exploring the Efficacy of Single-Atom Alloy Catalysts for the Haber-Bosch Process

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The Haber-Bosch process, which produces ammonia from its constituent elements, has been considered one of the greatest inventions in history due to its role in fertilizer-based food production and the population explosion in the 20th century.[1] The reaction, $N_2 + 3\ H_2 \rightarrow 2\ NH_3$, is industrially performed over Fe-based catalysts at high pressures (200-300 bar) and temperatures (400-500°C). The grandest energetic challenge in the Haber-Bosch process is the activation of the N_2 triple bond, which has been shown to be the rate limiting step both experimentally[2] and theoretically.[3] Catalysts for the Haber-Bosch process generally follow the universal Brønsted-Evans-Polanyi (BEP) trendline relations, which impose a limitation on a metal or metal alloy's catalytic abilities.[4-6] Thus, to design a novel catalyst that supersedes existing ones, we must break or circumvent the BEP trendlines.

Recently, a new class of catalysts has been designed for H_2 activation, where an active and isolated single atom sits within a host of inactive metal atoms.[7] These single-atom alloys readily dissociated H_2, dispersed the hydrogen atoms to the host metal, and did not bind the hydrogen atoms too strongly. Using density functional theory, we identified two different host metals (iron and cobalt) and four different active promoter metals (nickel, molybdenum, rhenium, and ruthenium) that could be employed in unison for N_2 activation. Our results show that cobalt and molybdenum work in combination to reduce the N_2 activation barrier, disperse the individual nitrogen atoms, and not bind the nitrogen atoms too strongly so they could be reduced to NH_3. Then, using microkinetic modeling, we found that the Mo-promoted Co single-atom alloy improves the production rate of ammonia, which could lead to a considerable enhancement of current industrial Haber-Bosch catalysts.

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7. Insights into Nitrate Degradation over Indium-Decorated Palladium Nanoparticle Catalysts

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Nitrate (NO_3^-) is a ubiquitous groundwater contaminant, and is detrimental to human health. Bimetallic palladium-based catalysts have been found to be promising for treating nitrate (and nitrite, NO_2^-) contaminated waters. Those containing indium (In) are unusually active, but the mechanistic explanation for catalyst performance remains largely unproven. We report that In deposited on Pd nanoparticles (NPs) ("In-on-Pd NPs") shows room-temperature nitrate catalytic reduction activity that varies with volcano-shape dependence on In surface coverage. The most active catalyst had an In surface coverage of 40%, with a pseudo-first order normalized rate constant of k_{cat} ~ 7.6 L $g_{surface-metal}^{-1}$ min^{-1}, whereas monometallic Pd NPs and In_2O_3 have nondetectible activity for nitrate reduction. X-ray absorption spectroscopy (XAS) results indicated that In is in oxidized form in the as-synthesized catalyst; it reduces to zerovalent metal in the presence of H_2 and re-oxidizes following NO_3^- contact. Selectivity in excess of 95% to nontoxic N_2 was observed for all the catalysts. Density functional theory (DFT) simulations suggest that submonolayer coverage amounts of metallic In provide strong binding sites for nitrate adsorption and they lower the activation barrier for the nitrate-to-nitrite reduction step. This improved understanding of the In active site expands the prospects of improved denitrification using metal-on-metal catalysts.

8. H_2O-Improved O_2 Activation on the Pd–Au Bimetallic Surface

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To extend our understanding of the O_2 activation properties of the Pd–Au surface, we have prepared Pd–Au (111) model catalysts in ultrahigh vacuum in order to investigate the interaction of H_2O with adsorbed O_2. Molecular oxygen mostly desorbs from the Pd–Au surface between 80 K and 180 K, but when co-adsorbed with H_2O the O_2 desorption behavior changes markedly with O_2 evolving between 150 K and 190 K. Thus, the adsorbed O_2 molecules are more strongly bound via the interactions with H_2O on the Pd–Au surface, and this interaction leads to large enhancements in the dissociation of O_2 as determined *via* the generation of CO_2 upon exposure to CO at 250 K in reactive molecular beam scattering measurements (CO-RMBS). These results demonstrate the improved activation of O_2 by H_2O on the Pd–Au surface, and are likely applicable to various oxidative reactions on Pd–Au bimetallic catalysts.

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9. A New Approach To Predict Accurate Adsorption Energy From Mainstream Density Functionals

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The popularity of density functional theory (DFT) in surface science and heterogeneous catalysis research relies on the accuracy of the DFT exchange correlation functional. The prediction of adsorption energies, i.e. the interaction energy between molecules and solid surfaces, is an integral part of theoretical studies of catalytic chemical reactions and its accuracy is essential. However, many mainstream density functionals give erroneous prediction for the atoms/molecules whose adsorption is dominated either by chemisorption or van der Waal (vdW) interactions. In this work, we present a new method that accurately predicts the adsorption energies which is based on DFT calculations with periodic boundary conditions using adaptively weighted sum of energy from RPBE and optB88/optB86b vdW functionals. We compared our method predicted adsorption energies against a set of published 39 experimental calorimetric measurements.[1] Our results show that this method has better mean absolute error (MAE) and root mean squared error (RMSE) of 13.4 and 19.3 kJ/mol respectively,[2] compared to MAE and RMSE of 20.4 and 26.4 kJ/mol of BEEF-vdW functional.[2] Hence this method can accurately predict adsorption energies regardless of whether the adsorption processes are dominated by chemisorption or dispersion forces, and produces superior accuracy to any current standard DFT functional alone.

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10. Ag-Promoted Dehydroaromatization of Ethylene to Aromatics over ZSM-5 Catalysts

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Industrial production of aromatics heavily relies on catalytic reforming in refineries.[1] Driven by the limited supply of fossil fuels and the recent shale gas revolution, it is highly desirable to develop methane- and/or light olefin-based processes to meet the growing demand for aromatics. Ethylene dehydroaromatization (DHA) over Ag-ZSM-5 is one of the promising technologies given the availability of ethylene feedstock. In addition, Ag-ZSM-5 was reported to promote aromatic selectivity from isobutane aromatization.[2] Here, we present a systematic study on the influences of Ag species and methane co-feed on ethylene DHA over Ag-ZSM-5. It was observed that Ag-ZSM-5 exhibits enhanced aromatic selectivity (~60%) than H-ZSM-5 (~20%) at similar ethylene conversion (at 400 °C and 1 atm) in the absence of methane co-feed.[3] Interestingly, both Ag- and H-ZSM-5 show very similar catalytic behaviors when methane was co-fed. Conversely, methane is activated over Ag-ZSM-5 with $\leq$ 5% conversion, whereas H-ZSM-5 is inactive in methane conversion. These observations are qualitatively consistent with density functional theory (DFT) results that compare activation barriers and adsorption energies of ethylene and methane over H- and Ag-ZSM-5. Collectively, these studies seek to improve the design of heterogeneous catalysts for non-oxidative upgrading of methane and light olefins.

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11. Metal Oxide Supported Gold Nanocatalysts: Synthesis and 1-Octyne Adsorption Studies

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Gold nanoparticle catalysts possess high selectivity in some hydrogenation reactions, making them potentially useful industrial catalysts; however, these catalysts typically are not very active. Several factors affect Au catalyst activity, including the number of active sites, support effects, and electronic differences across the metal particles. To better understand the mechanism of alkyne hydrogenation and the effects of the underlying support on supported Au catalysts, several metal oxide were synthesized using various sol-gel methods. Surface area and average particle sizes were determined by nitrogen adsorpiton and Brunauer-Emmett-Teller theory. Gold nanoparticles were prepared using a colloidal synthesis technique and deposited on the supports via spontaneous adsoprtion. Alkyne adsorption onto the catalysts was studied through FTIR spectroscopy using 1-octyne. Synthesis conditions and trends in alkyne binding will be reported and discussed.

12. Transition Metal-Doped Rare-Earth Oxysulfide Catalysts for High Temperature Dry Reforming of Methane

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The purposes of our work are to acquire a "proof of principle" data set towards the development of sulfur- and water-tolerant (especially the former) transition metal-doped rare-earth oxysulfide (TM-REO) catalysts for high temperature reforming, and develop a mechanistic rationale for how surface sulfidation alters reforming and coke formation kinetics. Experimental reactivity studies using feeds characteristic of methane dry reforming are used to identify doped TM-REO (e.g., Mn/Ce-La or Ni/Ce-Zr) systems that are tolerant of sulfur and water at realistic levels, an extension of our previous work on tar reforming. To date, we have tested different TM (Ni, Mn, Fe)-doped Ce/La and Ce/Zr catalysts at 725-775℃ for dry reforming and combined dry/steam reforming. Future work will focus on evaluating the catalytic performance in the presence of sulfur poisons.

13. Pd/ZSM-5 Catalysts as Passive NOx Adsorbers for Automotive Emission Controls

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Reducing cold-start emissions, emissions under 200 °C, will play a significant role in meeting future EPA and EU emissions standards. By adsorbing NO and NO2 at low temperatures and releasing these gases in temperatures regimes where traditional emission control catalysts can operate, Passive NOx Adsorbers (PNAs) augment existing emission control systems and are a promising new field of catalysis.

Four catalysts – 0 wt% Pd, 1wt% Pd, 1 wt% Pd/1 wt% Fe, and 2 wt% Pd, were washcoated onto a 0.25in diameter, 2in length, 600 cspi monolith cores at a fixed loading of 1.5 g/in^3. NO uptake was measured over a five minute period through FTIR spectroscopy. NO adsorption was accompanied by noticeable NO2 slip from the catalyst. The addition of Fe to the catalyst composition significantly improved the performance of NOx uptake.

NOx desorption showed complex behavior. Over half of desorbed NOx occurred in the form of NO2. As NO adsorbs as a mono nitrosyl palladium complex, this shows that NO is being converted into NO2 through a zeolite-surface reaction and likely storing on the Pd-less acid sites of the zeolite and binder.

14. Rational Catalyst Design for HDO on MoO$_3$(010): Computational Screening and Machine Learning for Discovery of New Promoter Materials

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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.[1-2] We used a realistic MoO$_3$(010) facet obtained from an ab-initio thermodynamic phase diagram calculated under reaction conditions to investigate its suitability as a HDO catalyst. HDO requires the initial creation of a vacancy site where the feed molecule can adsorb. However, the oxygen vacancy formation on MoO$_3$(010) is slow (high activation barrier) and highly endothermic. This scenario is reminiscent of HDS on MoS$_2$,[3] 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 as 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. We are in the process of adding machine learning techniques, such as principal component analysis, to expand our computational screening search space and discover promoter materials across all transition, alkali and alkaline earth metals. With this approach, we aim to predict ab-initio/experimental reactivity trends, only by using intrinsic physical properties of promoter materials used in the screening study. 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.

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15. Hydrogen Activation and Mobility on Au/TiO_2(110) in the Limit of Low Water Pressure

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Proton transport is paramount in a wide range of fields spanning biology, chemistry and catalysis,[1,2] and studies involving proton transport on the hydrated surface of oxides are gaining increasing interest lately.[3] Of particular interest to our work is the role of proton-assisted reaction steps during selective oxidation reactions as recently reviewed by Tran *et al.*[4] Under the right conditions, mixtures of H_2, O_2, and H_2O may form reaction intermediates that mimic those derived from H_2O_2, a potent and green chemical oxidant. This type of chemistry is dominantly reported for Au/TiO_2 catalysts at low temperatures, and the interplay between active sites on the metal and the oxide support plays a crucial role in reported mechanisms for CO oxidation,[4] hydrocarbon oxidation[5] and the water-gas shift reaction.[6]

Herein, we present a comprehensive density functional theory study of the activation of H_2 at the interface of gold nanoparticles and rutile TiO_2(110) support. The Au/TiO_2 interface sites are found to be the most active sites for heterolytic H_2 dissociation, demonstrating their critical role. The role of bridging and terminal hydroxyl groups on TiO_2(110) during proton diffusion is also examined in the limit of low water pressures. Proton diffusion along the [001] direction was found to be significantly easier than along $[1\bar{1}0]$ direction, leading to anisotropic properties for proton transport. The findings of this study provide a directive for the catalyst design with preferred orientation of gold particles with respect to the TiO_2(110) surface to enhance the desired reactant transport depending on the particular catalytic system requirements. Thus, studying H_2 activation and its mobility yields useful information for the effective design of Au/TiO_2 catalyst making it competitive with current catalysts for reactions involving hydrogen.

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16. Rational Design of Nanoporous Zeolite Material through Molecular Design and Mechanistic Study of Nucleation and Growth

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Microporous zeolites have garnered much attention due to the growing opportunities for their use in a wide range of applications spanning energy to medicine. Despite their extensive use in commercial processes, an understanding of their growth mechanism(s) remains elusive. The rational design of zeolite materials calls for more versatile synthetic approaches capable of a priori tailoring crystal properties, such as crystal size, and morphology.

To this end, we have taken a multifaceted approach of first developing the understanding of zeolite crystallization, which in turn can be used to develop generalized design platforms for controlling physicochemical properties of crystals with varying topology. We will present mechanistic studies of zeolite frameworks LTL *(1, 2)*, CHA *(3)*, MFI *(4)*, and LTA. Using a variety of techniques, we examined the time-resolved transformation of bulk amorphous precursors in LTL and CHA synthesis to their crystalline phase. However, techniques used in these studies have the inherent drawback of being invasive during sample analysis or preparation. To avoid this problem, we studied MFI and LTA crystallization using non-invasive in-situ atomic force microscope (AFM). We used this state-of-the-art tool to monitor the growth of zeolite surfaces by nonclassical mechanisms (e.g., nanoparticle attachment) under solvothermal conditions.

In the light of dual growth mechanism, we studied zeolite crystallization in the presence of zeolite growth modifiers (ZGMs), which are molecules that selectively bind to specific surfaces of zeolite crystals and mediate anisotropic growth rates and/or control aggregation of bulk precursors. We systematically examined a library of modifiers ranging in their structure and functional moieties to assess the physicochemical properties that regulate their efficacy and specificity. We demonstrate that the judicious selection of ZGMs can markedly alter zeolite crystal morphology and size for LTL and SSZ-13 (often modifying size over 3 orders of magnitude). Collectively, these studies seek to establish general heuristics for designing zeolites with tailored properties. This facile, economical method is unmatched in its ability to tune SSZ-13 and LTL crystal size. 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.

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17. CO, C_2H_2, and C_3H_6 Oxidation on Pd/Ceria-Zirconia/Alumina Three-Way Catalysts

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Three-way catalyst (TWC) light-off (LO) performance is critical in cost effectively meeting automotive emission standards. Improvements in catalyst LO should include lower precious group metal (PGM) loading, use of a lower cost PGM such as Pd, and catalyst modifications and components that minimize inhibition effects of exhaust species and enhance catalyst activity. The use of ceria-zirconia (CeO_2-ZrO_2) within the TWC provides the key benefit of oxygen storage, compensating for deviations from stoichiometric operating conditions by supplying oxygen for CO and HC oxidation under rich transient conditions. The light-off (ignition) and isothermal, steady-state behavior for individual oxidation and co-oxidation of CO, C_2H_2, and C_3H_6 under near-stoichiometric conditions was studied using a Pd/Ceria-Zirconia/Alumina monolith catalysts. CO, C_2H_2, and C_3H_6 were observed to be self–inhibiting. CO LO temperatures decreased with increasing catalyst ceria content. Mutual inhibition effects were also examined for mixtures of CO and C_2H_2 and CO and C_3H_6. Steady-state kinetics measurements during individual species oxidation were conducted to find reaction orders and activation energies of oxidation.

18. Crystallization of One-dimensional Zeolites by Nonclassical Pathways

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Zeolites are microporous materials that are heavily utilized in commercial applications such as catalysis, separations, ion exchange, and adsorption, among others. Their utility is based largely on their unique characteristics that include excellent stability, well-defined networks of pores, and tunable physicochemical properties (i.e., shape, size, and composition). Despite significant effort to understand the formation of zeolites,[1,2] their pathways of growth are not well understood owing to complex nonclassical mechanisms involving the assembly of precursors. For example, syntheses commonly lead to the formation of *worm-like particles* (WLPs), which are bulk amorphous precursors that serve as putative growth units during crystallization[3]. Evidence of crystallization by particle attachment (or CPA) is mounting for a range of materials that include biominerals[4], metal oxides[5], and zeolites[6]. Here, we will discuss the pathways of formation for two one-dimensional zeolites (LTL and TON types). We will discuss the results of standard synthesis protocols that incorporate crystal seeds and/or zeolite growth modifiers (ZGMs), which are molecules that alter the anisotropic growth rate(s) of zeolite crystallization. The results presented here focus on fundamental aspects of zeolite nucleation and growth, as well as describing how we can capitalize on this knowledge to rationally design materials with superior performance than those derived from conventional synthesis methods.

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19. First-principles Kinetic Monte Carlo Simulations For Heterogeneous Catalysis: Hydrodeoxygenation of Acetaldehyde on Ru/TiO_2(110)

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Catalytic upgrade of bio-oil to fuels and chemicals requires the selective reduction of its 28-40 wt% oxygen content while avoiding undesired C-C bond cleavage reactions. Using first-principles kinetic Monte Carlo (kMC) simulations, we first investigated the reduction properties of Ru/TiO_2 and then analyzed the hydrodeoxygenation (HDO) pathways for acetaldehyde. Acetaldehyde was chosen as a probe molecule, because it is a small compound suitable for *ab-initio* work, but contains both a C-O and a C-C bond, allowing us to study selectivity preferences. First-principles kMC is a multiscale modeling approach that extends atomic-scale energetic information obtained from density functional theory (DFT) to realistic time and length scales. A key advantage of kMC over more traditional microkinetic modeling is that it explicitly considers correlations, fluctuations, and spatial distributions of the chemicals on catalyst surface.

Commonly proposed HDO mechanisms on oxide materials invoke oxygen vacancy sites as catalytically active sites, but the mechanism of their formation remains disputed.[1] To address this issue, we used prior DFT data from our group and are developing a sophisticated kMC model with three distinct regions that represent metallic Ru, the TiO_2 support and the interface between them. Our results show that rutile TiO_2(110) with defect-free, stoichiometric surface termination can hardly be reduced with hydrogen treatment. The presence of Ru nanoparticles, however, dramatically increase the reduction rate of the TiO_2(110) surface. Furthermore, our preliminary results indicate that large, metallic Ru particles preferentially catalyze hydrogenation rather than the direct deoxygenation (DDO) or decarbonylation (DCN) reactions. In future work we aim to develop a detailed HDO mechanism on Ru/TiO_2 and other oxide supported metals that accounts for the spatial distribution of active sites and can elucidate the role of interfacial sites. Ultimately, our results will contribute valuable information to the understanding of the complex mechanistic interplay of reaction steps during HDO over oxide supported metal catalysts.

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20. Palladium Dendron Encapsulated Nanoparticles Supported on MCM-41 and SBA-15

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The synthetic approach of dendrimer-encapsulated nanoparticles (DENs) leads to well-defined sizes, compositions and structures of nanoparticles controlled by the dendrimer template[1]. In this work, melamine dendrons tethered to ordered mesoporous silica (OMS) were used to form palladium nanoparticles. Numerous methods including X-ray diffraction, infrared spectroscopy, thermal gravimetric analysis, ultraviolet–visible spectroscopy, nitrogen porosimetry, and scanning transmission electron microscope (STEM) have been used to characterize the hybrid materials step by step. The STEM images show the formation of uniformly sized palladium particles with a mean size of 1.8 nm. The accessibility of both the metal sites and dendron ligand sites were demonstrated by catalytic probe reactions and CO_2 uptake experiments. Heck reaction results show that the encapsulated palladium particles are catalytically active while the Nitroaldol (Henry) reaction shows that the amine sites are catalytically active in the palladium-containing samples. Carbon dioxide uptake measurements showed minimal perturbations to the CO_2 uptake formation of palladium particles. These hybrid materials have potential uses in reactions where both the organic and metal center can be used sequentially such as Cascade reactions.

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21. Impact of Hydrocarbon Trapping on Temperature Programmed Oxidation over a Pt/Pd/BEA Monolith Catalyst

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The function of the diesel oxidation catalyst (DOC) comprising a washcoat of Platinum (Pt) and Palladium (Pd) (PGM = precious group metals) is to catalyze the oxidation of diesel effluent mixture of CO and hydrocarbons (HCs) with sufficiently high conversion. However, during the "cold start" a fraction of the exhaust hydrocarbons may escape unreacted[1]. A large-pore zeolite such as Beta (BEA) is added to the DOC to trap diesel exhaust hydrocarbons during the cold start. Although extensive research has been conducted on the BEA storage capacity, there is a need to gain insight on how BEA affects the performance of HC light-off (LO) and of the HC oxidation transient performance[2]. We conducted a typical experiments trapping experiment followed by the temperature programed oxidation, and dynamic-hysteresis analysis to gain a deeper understanding of functioning of the HC trap and to enable improved trap design and operating strategy. Unusual CO_2 formation spikes were observed during the oxidation of HC that was pre-stored on the catalyst before exposure to the temperature ramp. The c-OFDR measurements enabled construction of a 3-D contour plot of temperature versus time and position. The temperature spikes correlate with the measured CO_2 yield spikes. In the hysteresis analysis during cooling, the non-isothermal nature of this adiabatic system suggests that HC trapping and oxidation dominates in the different regions in the catalyst. Since the downstream is much hotter than the upstream, the HC is re-trapped by BEA at the upstream and the HC is drastically oxidizes at the downstream. Both events greatly consume the C_{12}, helping to reduce C_{12} emission, and lead to a much lower extinction temperature. Even at such low heating/cooling rate of ±1 °C/min, a significant counter-clockwise hysteresis behavior still exists. This study is the first to provide insight into the spatiotemporal features of transient behavior of HC trapping and oxidation of BEA/DOC catalysts, and also the first discovery of multiple HC LO phenomena.

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22. Mo-doped NiSe nanowire: Bifunctional Electrocatalyst with high Turnover Frequency

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Development of efficient, stable, and low cost bifunctional electrocatalysts for water splitting is essential for renewable and clean energy technologies. Herein, we report a facile hydrothermal method to synthesize Mo-doped NiSe nanowire on nickel foam (Mo-NiSe/NF) as bifunctional electrocatalyst for overall water splitting. The Mo-NiSe/NF exhibited excellent electrocatalytic performance and remarkable stability for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in alkaline condition (1 M KOH). To achieve current density of 10 $mA\cdot cm^{-2}$, a very small overpotential (η) of 115 mV and 270 mV was required for HER and OER, respectively. More importantly, the Mo-NiSe/NF possess high Turnover Frequency (TOF) value of 1.53 H_2 s^{-1} (η=200 mV) and 0.4 O_2 s^{-1} (η=310 mV) which demonstrate its high performance. This highly active and stable bifunctional electrocatalyst enables the overall water splitting in an alkaline solution under a cell voltage of 1.6 V to deliver 10 $mA\cdot cm^{-2}$.

23. Tailoring the Morphology and Active Site Distribution of ZSM-5 Catalysts

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The presence of micropores in zeolites often imposes severe mass transport limitations and adversely affects their catalytic activity. Here, we present a novel approach to tailor ZSM-5 crystallization using zeolite growth modifiers (ZGMs), which can bind to specific crystal surfaces and alter the anisotropic growth rates as a means of tailoring crystal habit.[1,2]

The unique properties of ZSM-5 catalysts, such as hydrothermal stability and shape-selectivity, are ideal for many reactions. Catalyst performance is dependent upon its chemical composition. A phenomenon known as “Al zoning” within ZSM-5 crystals has been reported in many studies; however, its origin is elusive.[3] To address this challenge, we have performed parametric investigations to assess the role of synthesis conditions on Al siting. Our findings reveal the ability to selectively tune the spatial distribution of Al in ZSM-5 to achieve more efficient catalysts for targeted reactions.

The ability to design ZSM-5 catalysts with tunable morphology and Al distribution opens new avenues for tailoring catalyst performance, and understanding property-performance relationships. ZSM-5 properties can be selectively optimized for a wide range of applications. To this end, this study provides a general platform for zeolite design and optimization that could potentially be applied to other framework types.

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24. Synthesis and Physico-Chemical Properties of ZSM5-supported Molybdenum Carbide Catalysts

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In the past decades there has been a growing interest in industry on the nonoxidative direct conversion of methane to higher transportable hydrocarbons, which can potentially enable efficient deployment of the vast natural gas sources (of which methane is the main constituent). Methane aromatization constitutes an attractive direct process that upgrades natural gas to benzene and hydrogen. The greatest challenge to the commercialization of this process is the rapid deactivation of the catalysts, consisting of Mo oxide supported on acid zeolites, mainly due to poisoning by coke formation, stemming from the presence of the acid sites on the support. Our work focuses on studying the active phase in the aromatization reaction, which is believed to be Mo carbide that is formed in situ, during an induction period, originating from the Mo oxides species[1-3] We have prepared catalysts consisting of Mo carbide with different loadings, supported on commercial ZSM5 zeolite and characterized their structure in order to determine the chemical and physical properties of these catalysts. Our results show that high loadings of Mo carbide can be supported on ZSM5 without introducing any relevant changes in the structure and surface area of the zeolite support.

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25. Plasmon-Induced Selective Carbon Dioxide Conversion on Earth-Abundant Aluminum-Cuprous Oxide Antenna-Reactor Nanoparticles

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The rational combination of plasmonic nanoantennas with active transition metal-based catalysts, known as ‘antenna-reactor’ nanostructures, holds promise to expand the scope of chemical reactions possible with plasmonic photocatalysis. Here, we report earth-abundant aluminum@cuprous oxide antenna-reactor heterostructures that operate more effectively and selectively for the reverse water-gas shift reaction under illumination than in conventional thermal conditions. Through rigorous comparison of the spatial temperature profile, optical absorptions, and integrated electric field enhancements of the catalyst, we have been able to distinguish between competing photothermal and hot-carrier driven mechanistic pathways. The antenna-reactor geometry efficiently harnesses the plasmon resonance of aluminum to supply energetic hot-carriers and increase optical absorption in cuprous oxide for selective carbon dioxide conversion to carbon monoxide with visible light. The transition from noble metals to aluminum based antenna-reactor heterostructures in plasmonic photocatalysis provides a sustainable route to high-value chemicals and reaffirms the practical potential of plasmon-mediated chemical transformations.

26. Synthesis and Characterization of Tin, Tin/Aluminum, and Tin/Boron Containing MFI Zeolites

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Zeolites are an intellectually fascinating and technologically important class of materials used in the chemical conversion and separation of small molecules. Their ability to achieve these unit operations is a result of the crystalline microporous structures enabling highly size-selective separations.[1] Coupling that with the ability to impart acidity to the zeolites through the introduction of trivalent elements such as aluminum and boron into the framework has led to zeolites finding a wide range of applications in the chemical and petrochemical industry.[2] Over the last 20-30 years beyond aluminum and boron, it has been shown that other elements including titanium[3], tin[4] and germanium[5] can be introduced into the zeolite lattice with varying levels of success. This expansion of the zeolite framework composition space has led to new uses for zeolites in a range of catalytic chemistries.

The synthesis and characterization of tin, tin/aluminum, and tin/boron containing MFI zeolites will be presented. It is shown that tin uptake is high (near 100%) and decreases with the introduction of a second heteroatom. Additionally, the zeolite crystals decrease in size and morphology changes with the introduction of a second heteroatom as evidenced by FE-SEM and XRD. UV-Vis confirms the tetrahedral framework coordination of tin within the zeolite and there is not evidence for SnO_2 given the absence of a strong signal at 280 nm. XPS, in consistent with UV-Vis, indicates the absence of an additional phase in the surface of these particles. Studies of methanol adsorption using in-situ IR spectroscopy indicate that tin-MFI sample with low tin contents possess lower acidic strength, and that tin/aluminum samples confirm aluminum within the zeolite through the presence of a Brönsted acid site.

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27. Optimizing ZSM-11 Catalysts for 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 yields 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 studies of ZSM-11 synthesis, specifically with respect to methods of tailoring 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, shape and Si/Al ratio. 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.

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28. First Principles Insight into the High Activity and Selectivity of Pd_3Cu Alloys for the Guerbet Reaction

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The Guerbet and related condensation reactions can be used to convert biomass-derived short chain alcohols into higher branched alcohols.[1] A variety of transition metal-based heterogeneous catalysts (e.g. Pd-based catalyst) possess good activity for this reaction, but the suppression of undesired side reactions must be further improved.[2] A newly discovered Pd-Cu alloy catalyst, however, was experimentally found to combine the activity of Pd with the selectivity of less active Cu, resulting in a unique catalyst with exceptional reaction rate and low tendency for the undesired decarbonylation reaction.[3] In this work, we present results from density functional theory simulations and micro-kinetic modeling that explain the origin of the remarkable properties of this bimetallic alloy catalyst in terms of synergistic alloying, segregation, coverage and particle size effects. We anticipate that other bimetallic alloys with tailored performance can be discovered based on the fundamental understanding contributed by this study.

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20. Promotional effects of Fe on Mo/HZSM-5 in Non-Oxidative Methane Aromatization

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Upgrading natural gas (of which methane is the main component) to aromatics has attracted much attention since Wang et al.[1] laid the groundwork in 1993 on non-oxidative methane aromatization, which converts methane to aromatic compounds and hydrogen, using MoOx supported on ZSM-5 as catalyst. Extensive investigation has been carried out on zeolite-supported molybdenum oxide catalysts in the past decades, however, the acid sites of the zeolite support, while indispensable for formation of the aromatic molecules by polymerization, also cause rapid catalyst deactivation due to formation of carbon deposits. This results in an important limitation that prevents commercialization of the aromatization process in industry. Our work involves investigating ways to inhibit deactivation by carbonaceous deposits by studying the effects of doping Mo/ZSM5 catalysts with different loadings of FeO_x (from 0.2 to 1 wt%). Our results show that adding a small amount of FeO_x (0.2% FeO_x) not only increases the stability of the catalyst, but also enhances its yield to the wanted product: benzene. The structural characterization of the spent catalysts indicates that addition of Fe, not only modifies the structure of the catalyst in reaction, but also influences the nature of the carbon deposits, which could account for the longer catalyst life.

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30. Zeolite Catalyst Design and Optimization: Impact of Synthesis Parameters on Crystal Properties

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Zeolites possess well-defined networks of pores that give rise to shape selectivity as catalysts for chemical reactions and provides an essential advantage for their use as sieves and sorbents in commercial applications. The performance of zeolite catalysts (i.e., activity and lifetime) is closely aligned with their physicochemical properties, which include (but are not limited to) shape, size, and composition. The design of zeolite catalysts *a priori* is challenging owing to the complexity of their synthesis that is derived from the multiple growth units and pathways of crystallization. Previous studies have demonstrated that zeolites, such as zeolite L (LTL type), grow via nonclassical mechanisms involving the assembly of so-called *worm-like particles* (WLPs), which are bulk amorphous precursors that serve as putative growth units during crystallization.[1] Evidence of crystallization by particle attachment (or CPA) is mounting for a range of materials that include biominerals[2], metal oxides,[3] and zeolites.[4] In this relatively new area of research, there are many knowledge gaps between the design of synthesis conditions, the resultant precursors, and the final physicochemical properties of the zeolite products. Here, we will discuss how the judicious selection of synthesis parameters, such as reagent sources, alkalinity, and supersaturation, alter the morphology and structure of crystalline products. Our findings reveal the involvement of diverse precursors and multifaceted crystallization pathways. The results presented here provide a generalized platform for ration design towards the development of optimal zeolite catalysts through facile, commercially viable synthesis approaches that bridge fundamental research with practical applications.

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31. Combining Plasmonic and Catalytic Metals into 'Antenna-Reactor' Nanostructures for Photocatalysis

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Metal nanoparticles traditionally used in heterogeneous catalysis, both in the lab and on an industrial scale, do not effectively couple with light. On the other hand, plasmonic metals such as Au, Ag, and Al, interact very strongly with light, but are often not suitable to drive diverse chemical reactions on their surfaces. Our solution is to develop modular 'antenna-reactor' nanostructures that decorate plasmonic 'antenna' Al nanocrystals with 3-5 nm catalytic 'reactor' transition metals islands. Here, eight varieties of Al-based antenna-reactor nanoparticles will be presented as a new class of plasmonic photocatalysts. Characterization using high-resolution electron microscopy, energy dispersive X-ray spectroscopy, and electron tomography were used to reveal the morphology and 3D nature of these materials. Photocatalytic studies have revealed that driving chemical reactions with photons, rather than heat, can introduce new hot-carrier driven mechanistic pathways. These hot-carrier driven reactions have shown to have potential for selective transformations, which in the context of the hydrogenation of acetylene showed increased selectivity of ethylene production over ethane by nearly 400%. The combination of plasmonic and catalytic metals into a single heterostructure is a promising route to new tunable photocatalysts in the future.

32. A Screening Study Based on Uncertainty Quantification of Methane Activation on Metal Exchanged Zeolites

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Zeolite catalysts are extensively used in petroleum refining, and metal exchanged zeolites are known to be active in the conversion of methane into higher hydrocarbons.[1] The chemical activation of methane, which has the highest H-to-C ratio of all hydrocarbons, presents itself as a difficult problem to solve because of its relative inertness and stability.[2] The rate-determining step in most methane conversion processes is the activation of CH_4. Theoretical investigations into this problem use different models which approximately describe the physics of a periodic zeolite unit cell in the form of simplified active site models. These models differ from each other and therefore, mechanistic information derived from these investigations are not necessarily indicative of the activation of methane taking place inside the zeolite pores.

In an attempt to bridge these inconsistencies in choice of model, we investigate the activation of CH_4 over metal exchanged Lewis acid species across three different zeolite models, a 5T cluster model, a periodic ZSM-22 unit cell and a periodic ZSM-5 unit cell using Density Functional Theory (DFT) calculations. Analysis of reaction energies and activation barriers showed that a simple and computationally efficient 5T cluster model mimics the trends in activity of more complex periodic ZSM-22 and ZSM-5 unit cells for CH_4 activation. A spread of ensemble energies obtained from our calculations were used to quantify the uncertainty in activating CH_4 over specific Lewis acid sites and make definitive predictions about the efficacy of the simple 5T cluster in describing trends in methane activation in metal exchanged zeolites.

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33. Fast Cycling in a Non-Isothermal Monolithic Lean NOx Trap Using H_2 as Reductant: Experiments and Modeling

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A combined experimental and modeling study of fast cycling NOx storage and reduction with H_2 for emissions control of lean burn gasoline and diesel vehicles is conducted to provide mechanistic insight and detailed understanding to Toyota's Di-Air technology [1]. Experiments reveal NOx conversion enhancement over a model $Pt/Rh/BaO/CeO_2/Al_2O_3$ Lean NOx Trap (LNT) catalyst for cycle times less than 10 s (fast cycling) compared to the longer cycle times typical of conventional NSR. Increased cycle frequency results in the increase (decrease) of the cycle-averaged NOx conversion (NH_3 selectivity) over a wide temperature range. The more frequent storage and regeneration of fast cycling increases the utilization of stored NOx capacity by decreasing NOx breakthrough during the lean phase. The decreased NH_3 selectivity is in part a result of a combination of increased efficiency of the NH_3 oxidation by oxygen stored by the ceria component and of the adsorption of NH_3 on the support. A global kinetic model incorporated into a non-isothermal 1-D monolith reactor is effective in capturing most of the experimental trends. Quantitative agreement requires treatment of the extent of mixing of the lean and rich feeds upstream of the reactor, as well as of mixing of the product stream in the downstream FTIR cell. The predicted axial temperature profile shows a front-monolith temperature rise as high as twice that measured in the middle-monolith under slower cycling. Under faster cycling a predicted 100 °C front-monolith temperature rise contrasts to a measured near-constant middle-monolith temperature. Non-isothermal effects are especially important when catalyst temperatures exceed 450 °C, which lowers the NOx storage capacity, resulting in an increased amount of slipped NOx during early lean phase.

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34. Y-doped CeO_2 Nanorod Catalyzed Oxidative Dehydrogenation of Cyclohexane and Cyclohexene

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Cerium oxide has attracted considerable attention in part to its redox behavior. CeO2 was shown to be good CO oxidation catalyst with proper engineering of surface oxygen vacancies. The tuning of the concentration of surface oxygen vacancies can be controlled by doping the cerium oxide with yttrium. The amount of oxygen vacancies is correlated with the catalytic activity. Y-doped cerium oxide nanorods were tested for the oxidative dehydrogenation of cyclohexane and cyclohexene, which involves a redox process. Other catalyst such as vanadium oxide requires a temperature of ~600 ^{0}C. In contrast, doped cerium oxide shows improved catalytic activity at lower the reaction temperatures to 150 ^{0}C with a cyclohexane conversion of ~20% and a product distribution of 38%, 11%, 1%, 50% for cyclohexene, benzene, 1,3-cyclohexanediene and combustion products, respectively.

35. Understanding the Role of H_2O in the Preferential Oxidation of CO in H_2 Using Kinetic Studies of H_2 Oxidation

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Supported Au nanoparticles are known to be excellent CO oxidation catalysts and poor hydrogenation catalysts. Surprisingly, however, they are not sufficiently selective for the preferential oxidation of CO in hydrogen (PrOx) to be industrially useful. During CO oxidation, we have showed that molecular O_2 is activated by a proton transfer from H_2O, which in turn speeds up the CO oxidation reaction.[1] In the current study, we investigated the role H_2O plays in the H_2 oxidation reaction, in order to better understand the factors that control activity and selectivity in PrOx.

By studying the kinetics of the H_2 oxidation reaction, several important observations were made. Firstly, under PrOx reaction conditions, H_2 was nominally 0th order at all H_2O coverages, similar to CO in the CO oxidation reaction. Secondly, O_2 has a weakly positive order (0.2-0.4) under all H_2O coverages, which is also similar to the O_2 order in CO oxidation. Thirdly and most importantly, the hydrogen oxidation reaction had a large negative H_2O reaction order (-0.65 for TiO_2 and -0.7 for Al_2O_3), indicating higher H_2O coverages inhibit the H_2 oxidation reaction. This suggests the same O_2 intermediate (Au-OOH) is involved in both reactions, but that H_2 and CO are activated at different sites on the Au catalysts.

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36. Selective Oxidation of Ring-Locked Glucose Using Pd-on-Au Catalyst

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A popular approach to upgrade lignocellulosic biomass is to depolymerize it and to recover glucose as feedstock for other chemicals. The selective oxidation chemistry of glucose is difficult to control because of the high reactivity of multiple hydroxyl groups and the hemiacetal group. Ring-locking is a concept to functionalize glucose at its anomeric carbon (C-1) and to enhance its ring structure stability. In recognizing that glucose dehydration to levoglucosan occurs highly selectively under pyrolytic conditions after the ring structure is chemically locked, we studied the oxidation behavior of similarly ring-locked glucose using Pd and Au NPs, and bimetallic Pd-on-Au NPs. These model catalysts are carbon supported 4 nm Pd and Au NPs, and 4nm Pd-on-Au NPs with the surface coverage (sc) from 30% to 300%. The series of Pd-on-Au/C materials exhibited volcano-like catalytic activity dependence on Pd surface coverage with the optimal initial turnover frequency (TOF) 413 h-1 achieved near 80 sc% Pd that was >5 times more active than monometallic Au/C and Pd/C. Methyl-glucuronide is the dominant product formed with the around 50% selectivity for all the compositions. Without ring-locking, the selectivity to glucuronide is 0 under the same reaction condition. These findings demonstrate the ring-locking concept can be applied to glucose catalytic oxidation reaction to improve the selectivity of C-6 oxidized product.

37. Theoretical Investigation of Dephosphorylation of Organophosphates on CeO_2(111)

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Phosphorous is an essential building block for life on earth and is critical for food production. On the one hand, mineral phosphorous is a nonrenewable resource, while on the other hand, excessive dumping of phosphorous in the form of organophosphates due to modern agriculture is jeopardizing water resources around the world, including the Gulf of Mexico. Therefore there is an urgent need to recover and/or remove phosphorous from waterbodies. Natural degradation of organophosphates can take months and even years because the hydrolysis of the P-O ester bonds by microbes is the primary pathway [1]. Recently, Janos et al. suggested that cerium dioxide can promote the dephosphorylation of organophosphates [2]. Manto et al. studied the catalytic dephosphorylation of a model phosphate monoester using different shape-defined ceria nanoparticles and found nano-octahedra, which primarily exposes the (111) facet, to possess high catalytic activity for this reaction [3]. We are performing density functional theory calculations to understand the mechanisms of the dephosphorylation of organophosphates on ceria surfaces and how different organic groups affect the catalytic activity. The results will help establish the range of organophosphates for which ceria is effective at catalyzing dephosphorylation at ambient conditions, and shed light on how to further improve the effectiveness of ceria for this important reaction.

[1] B.K. Singh, A. Walker, *Fems. Microbiol. Rev.* 30 (**2006**) 428-471.

[2] P. Janos et al., *J. Rare. Earth* 32 (**2014**) 360-370.

[3] M.J. Manto, P.F. Xie, C. Wang, *ACS Catal.* 7 (**2017**) 1931-1938.

38. Bimetallic Metal Phosphide for Efficient Electrocatalytic and Photoelectrochemical Water Splitting

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Developing efficient and stable electrocatalyst for water electrolysis for the production of clean and renewable hydrogen fuels is a critical step of several clean-energy technologies. Transition metal phosphides have already been demonstrated to be highly active electrocatalysts for the hydrogen evolution reaction, oxygen evolution reaction and overall water splitting. However, the current fabrication methods for TMPs require harsh conditions with toxic gaseous chemicals, and offer little control over the metal-phosphorus stoichiometry, phase purity and electronic conductivity. Recently, we developed a facile and scalable strategy to develop highly active bimetallic FeMnP with a single source metal organic chemical vapor deposition (SSP-MOCVD) method. By taking the advantages of the SSP-MOCVD method, FeMnP can be easily deposited on various three-dimensional substrates including conductive substrate graphene protected nickel foam, Fluorine-doped Tin oxide glass (FTO) for water electrolysis and semiconductor substrate TiO_2 nanorod array for photoelectrochemical oxygen evolution. We systematically discussed the underlying mechanism supported by experimental results and theoretical calculations. The present SSP-MOCVD method provides an efficient approach for the fabrication of highly active electrodes for the use of solar energy.

39. Copper Nanoparticles for Plasmonic Photocatalysis: Carbon Dioxide Fixation and Reduction

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Reverse water gas shift (RWGS) reaction ($CO_2 + H_2 \rightarrow H_2O + CO$) could, in principle, be a promising way to convert the CO_2 into value-added chemical and mitigate the Greenhouse effect, but requires high temperature to achieve high conversion with thermal catalysis as it is an endothermic reaction with $\Delta G = +41$ kJ/mol. In this context, plasmonic photocatalyst, which photocatalyzes chemical reactions by transferring hot carriers derived from the decay of localized surface plasmon resonance (LSPR) to adsorbed molecules and activating their dissociation, might provide a preferable solution. Here we report a copper-based plasmonic photocatalyst showing high external quantum yield (~50%) for rWGS reaction under medium light intensity (~8 W/cm2) and ambient conditions. The photocatalysis exhibits high selectivity towards CO, high one-run conversion of ~ 50% and good stability, all outperforming the thermocatalysis. We quantified the photothermal effect through a combination of experimental measurement of surface temperature and COMSOL simulation of 3D-temperature-distribution of sample under light illumination. The plasmonic photocatalysis is further deconvoluted to get the contribution of hot-electron-driven chemistry, which shows superlinear-power-dependence with unique decreasing power law. We proposed a thermal-hot-electron mechanism, based on which the theoretical calculation gives the quantum yield of effective hot electron the same trend.

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(2) Mukherjee, S.; Zhou, L.; *et. al. J. Amer. Chem. Soc.* 136 **(2014)** 64-67.

40. Fast Cycling to Achieve High NOx Conversion in Lean Exhaust: Role of Ceria

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The abatement of NOx ($NO+NO_2$) remains a challenge under the continuously more stringent emission standards. Toyota researchers recently invented a new deNOx system, Di-Air (diesel NOx aftertreatment by adsorbed intermediate reductants), which involves fast injection of fuel into the exhaust feed to the NSR converter [1]. Data suggest that NOx conversion occurs the reaction of an intermediate produced through the reaction with O_2 and NO [1, 2]. However, a recent study [3] suggests that catalysts containing ceria may involve an alternative pathway of NOx conversion via NO decomposition at high temperatures. We studied in a bench-scale flow reactor system the NO decomposition and reduction on ceria under different frequencies with CO as sole reductant. NO, O_2, H_2O and CO_2 were introduced into the system to simulate lean exhaust. When lean/rich switching operation is applied, NO conversion increases compared to that obtained in steady state experiments. Also, an optimal lean/rich switching frequency can be found for different reaction conditions (e.g., temperature and feed condition). This study on NO decomposition on ceria during lean and rich cycling helps explain the beneficial function of ceria on NOx reduction at high temperatures, which also provide guidance for optimization of catalyst formulation and operation strategies.

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[2] Y. Zheng et al., Catal. Today, 276 (2016), 192-201.
[3] Y. Wang et al., Top. Catal., 59 (2016), 854-860

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_4 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).**