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2018 SPRING SYMPOSIUM

Friday, April 20, 2018

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The SWCS officers and I welcome you to the 2018 SWCS Spring Symposium, Friday, April 20, 2018, at the Grand Hall in the Student Center of Rice University (6100 Main Street, Houston, TX 77005).

We are delighted to present six invited speakers and 38 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 2018 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 up registration, pre-register via the following link is recommended:

<https://www.eventbrite.com/e/southwest-catalysis-society-2018-spring-symposium-tickets-44406529124>

To make registration easy, we only accept credit cards (Visa, MasterCard, Discover, and American Express) for the registration fee. For corporate donations, check, credit cards or on-line transfer are all welcome. Event ticket will be automatically generated and sent via e-mail. So please be prepared to input your e-mail address into the system when you pay.

PARKING: The best place to park is in the Central Campus Garage (See P3 for map.)

We hope to see you at the Symposium!

Lin Luo

The Dow Chemical Company
Chair



2018 PROGRAM

All talks, coffee breaks, lunch, and the poster session will be held in the Grand Hall at Rice.

- 7:30 AM** **Registration – Sheima Khatib, Director**
- 8:10 AM** **Welcoming Remarks – Lin Luo, Chair**
- 8:15 AM** **Jingguang Chen, Columbia University, Department of Chemical Engineering**
Converting CO₂ via Thermocatalysis and Electrocatalysis
- 9:00 AM** **Alex Katz, UC Berkeley, Department of Chemical and Biomolecular Engineering**
Environment on metal surfaces affects catalysis involving hydrogen transfer: insights from a uniform supported molecular catalyst obtained through a combination of precise synthesis, spectroscopy, kinetics, and electronic structure calculations
- 9:45 AM** **Coffee Break**
- 10:00 AM** **Kathy M. Keville, ExxonMobil Chemical Company**
2017 Winner of the SWCS Excellence in Applied Catalysis Award
ExxonMobil Catalyst Manufacture: A Rich History of Catalyst Discovery, Development, and Deployment
- 10:45 AM** **Southwest Catalysis Society Excellence in Applied Catalysis Award, Jeff Rimer, Award Selection Committee**
- 11:00 AM** **Lunch Break (Catered) and Poster Session**
- 1:00 PM** **In Memory of Jim Richardson**
- 1:05 PM** **Bob Davis, University of Virginia, Department of Chemical Engineering**
Selective Catalytic Oxidation of Alcohols over Supported Metal Nanoparticles and Atomically-Dispersed Metal Cations
- 1:50 PM** **Victor Johnston, Celanese Corporation**
Using Catalysts to Create Differentiated Performance in the Production of Chemicals
- 2:30 PM** **Student Presentation, Dayne F. Swearer, Rice University, Department of Chemistry**
Plasmon-mediated Catalysis with Aluminum-based Nanomaterials and Detection with THz Rotational Spectroscopy
- 2:50 PM** **Poster Awards, Nataly Garcia Vargas, Director**
- 3:00 pm** **Happy Hour at Valhalla, Rice University**
(Free beer provided, 6100 S Main St, Houston, TX 77005)
- 4:30 PM** **Adjourn**



Building numbers

Building Numbers:

21: Rice Memorial Center (student center) ___ meeting site

57: Central Campus Garage



Converting CO₂ via Thermocatalysis and Electrocatalysis

Jingguang Chen

Columbia University, Department of Chemical Engineering

Rising atmospheric concentration of CO₂ is forecasted to have potentially disastrous effects on the environment from its role in global warming and ocean acidification. Converting CO₂ into valuable chemicals and fuels is one of the most practical routes for reducing CO₂ emissions while fossil fuels continue to dominate the energy sector. The catalytic reduction of CO₂ by H₂ can lead to the formation of three types of products: CO through the reverse water-gas shift (RWGS) reaction, methanol via selective hydrogenation, and methane by the methanation pathway. In the current talk we will first describe our efforts in controlling the catalytic selectivity for the three products using a combination of DFT calculations and surface science studies over single crystal surfaces, catalytic evaluation of supported catalysts, and in-situ characterization under reaction conditions. Next, we will discuss our efforts in converting CO₂ without using H₂. This is motivated by the fact that ~95% of H₂ is generated from hydrocarbon-based feedstocks, producing CO₂ as a byproduct. We will present two approaches to avoid using H₂ for CO₂ conversion. The first approach involves the utilization of light alkanes, such as ethane, to directly reduce CO₂ via the dry reforming pathway to produce synthesis gas ($C_2H_6 + 2CO_2 \rightarrow 4CO + 3H_2$) and the oxidative dehydrogenation route to generate ethylene ($C_2H_6 + CO_2 \rightarrow C_2H_4 + CO + H_2O$). The second approach is the electrolysis of CO₂ to produce synthesis gas with controlled CO/H₂ ratios. We will conclude our presentation by providing a perspective on the challenges and opportunities in converting CO₂ via various routes in thermocatalysis and electrocatalysis.



Biography

Jingguang Chen is the Thayer Lindsley Professor of chemical engineering at Columbia University, with a joint appointment as a senior chemist at Brookhaven National Laboratory. He received his PhD degree from the University of Pittsburgh and then carried out his Humboldt postdoctoral research in KFA-Julich in Germany. After spending several years as a staff scientist at Exxon Corporate Research, he started his academic career at the University of Delaware in 1998 and rose to the rank of the Claire LeClaire Professor of chemical engineering and the director of the Center for Catalytic Science and Technology. He moved to Columbia University in 2012. He is the co-author of over 20 US patents and over 350 journal publications. He is currently the president of the North American Catalysis Society and an associate editor of *ACS Catalysis*. He received many catalysis awards, including the 2015 George Olah award from the American Chemical Society and the 2017 Robert Burwell Lectureship from the North American Catalysis Society.



Environment on metal surfaces affects catalysis involving hydrogen transfer: insights from a uniform supported molecular catalyst obtained through a combination of precise synthesis, spectroscopy, kinetics, and electronic structure calculations

Alexander Katz

University of California, Berkeley, Department of Chemical and Biomolecular Engineering

A longstanding mystery in catalysis on solid surfaces has been why oxygen treatment of a metal catalyst often promotes reactions involving hydrogen transfer such as hydrogenation, dehydrogenation, and hydrogenolysis. We wished to address the following questions: (i) if the role of oxygen in these systems is that of a ligand affecting catalysis involving hydrogen transfer on a metal surface, how does this work? and (ii) can other ligands also promote catalysis involving hydrogen transfer?

To investigate this, we have developed a uniform single-site catalyst model system that retains the stability of its metal frame in the presence of hydrogen as well as under hydrogenation conditions, as probed via in-situ X-ray absorption spectroscopy and infrared spectroscopy. It consists of a tetrairidium cluster, in which three of the iridium atoms – those on the basal plane that are each substituted with a single bulky calixarene ligand – are catalytically inactive and form a support for the active iridium atom at the apex of the tetrahedron. The observed extraordinary stability of this single-site catalyst is enabled by both the sterics of the calixarene ligands, which serve as the molecular equivalent of bumpers on a bumper car to prevent aggregation via coalescence, as well as the intrinsic stability of the tetrairidium cluster frame. This stability coupled with simple probe reactions allows us the ability to gain detailed knowledge of structure-function relationships in catalysis, and in particular here those involving oxygen as a sub-surface ligand on a metal.

We observe more than a 100-fold enhancement in ethylene hydrogenation activity after exposing our silica-supported tetrairidium cluster to dioxygen as a ligand. Raman spectroscopy uncovers the appearance of distinct bands that identify bridging peroxo ligands, consistent with prior crystal structures of oxygen interacting with diiridium clusters, during oxygen treatment of our supported catalyst. Dioxygen bonding to the electron-rich metal core persists even under hydrogen atmosphere and catalytic hydrogenation conditions, as demonstrated by infrared spectroscopy, which together with X-ray absorption spectroscopy quantifies the number of bridging peroxo ligands per cluster to be two. Both of these bridging peroxo ligands are bound to catalytically inactive basal-plane iridium atoms on the cluster – those immediately adjacent to the catalytically active apical iridium atom. The presence of these dioxygen ligands lowers the activation energy for ethylene hydrogenation by 4.8 kcal/mol relative to the same supported cluster catalyst in the absence of these dioxygen ligands; similar trends are observed with another reaction, involving simple hydrogen-deuterium exchange kinetics. Together with kinetic studies and electronic structure calculations, we demonstrate that the presence of dioxygen ligands on the basal plane results in a fundamental change in the atomic mechanism by which hydrogen transfer occurs. We also demonstrate how organic ligands on a metal surface can also control catalysis involving hydrogen transfer – for the same two reactions mentioned above. Altogether, our results speak to the importance of environment surrounding active sites, in affecting mechanisms of hydrogen transfer.





Biography

Alexander Katz is a leader in the molecular design, synthesis, and characterization of active sites for catalysis and adsorption, as controlled by the structure of molecular organic-inorganic interfaces. Alex began his career proving the first example of molecular design and control of solid acid-base bifunctional catalysis, consisting of anchored amines on an oxide support, using spectroscopic probes to determine the structure of the catalyst active site. He invented the composition of matter consisting of grafted calixarenes on oxides. The latter has allowed unprecedented control of environment as enforced by a macrocyclic ligand in Lewis acid catalysts (e.g., open versus closed). He has more recently brought this molecular control of catalysis structure and function to the realm of metal clusters, and has designed zeolite delamination without amorphization, and sites for selective adsorption of cations, and sugars for limiting biomass-related separations. He has founded Berkeley Materials Solutions, which is commercializing delaminated-zeolite catalysts, as well separations enabled via selective molecular recognition. Alex was born in Minsk, Belarus. He graduated University of Minnesota as a Bachelor of Chemical Engineering, Cum Laude in 1992 and a research M.S. in Chemical Engineering with Prof. Michael D. Ward as advisor. He was awarded a Fannie and John Hertz Foundation Fellowship for doctoral studies in catalyst synthesis and characterization with Prof. Mark Davis at California Institute of Technology in 1994, and later, in 1998, undertook postdoctoral studies in supramolecular chemistry at Institut Le Bel in Strasbourg, France, with Prof. Mir Wais Hosseini, as a NSF International Awards Postdoctoral Fellow. Alex began a multidisciplinary research program as Assistant Professor of Chemical Engineering at UC Berkeley in 2000, and has since been promoted to the rank of Professor. He was a Technion-Fulbright Fellow visiting professor at the Wolfson Department of Chemical Engineering in Haifa, Israel in 2008-2009. Seven Katz-group alumni have gone on to start their own research groups in academia around the world. Alex is the recipient of Hellman Family and 3M Young Faculty Awards, and a Young Scientist Prize from IACS (International Association of Catalysis Societies). He has also been recognized with numerous departmental and best engineering professor on campus teaching awards at Berkeley.



ExxonMobil Catalyst Manufacture: A Rich History of Catalyst Discovery, Development, and Deployment

Kathy M. Keville

ExxonMobil Chemical Company

ExxonMobil's contributions to zeolite catalysis span the entire technology pipeline from early stage research all the way through commercial manufacturing and customer support. Our expertise in catalyst manufacture has had a huge impact on the commercialization of step-out fuels, lubes, and petrochemical catalyst technologies. This presentation will highlight ExxonMobil's approach to the discovery, development, and deployment of zeolite catalysts. A specific emphasis on commercial catalyst manufacture will include zeolite synthesis, formulation, catalyst modification, calcination, and quality control. The development of these important catalyst technologies has been a key part of our history for the last 50 years and allows ExxonMobil and our customers to safely, efficiently, and reliably provide clean fuels, high quality lubricants, and important chemicals.



Biography

Kathy 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.



Selective Catalytic Oxidation of Alcohols over Supported Metal Nanoparticles and Atomically-Dispersed Metal Cations

Robert J. Davis

University of Virginia, Department of Chemical Engineering

Selective oxidation of alcohols to carbonyl compounds is an important reaction in organic synthesis and will likely play a significant role in the development of value-added chemicals from biomass. The industrial application of a precious metal catalyst such as Pt, however, can be hindered by deactivation and high price. We have therefore explored the mode of deactivation during alcohol oxidation on Pt by in-situ spectroscopy and studied the role of various promoters on catalyst performance. Results confirm that slow decarbonylation of product aldehyde deposited unsaturated hydrocarbon on the surface that blocked access to the active sites. Addition of Bi as a promoter did not prevent the decarbonylation side reaction, but instead enhanced the activation of dioxygen during the catalytic cycle. In an effort to avoid the use of precious metals altogether, the oxidation of alcohols over atomically-dispersed, non-precious metal cations (Fe, Cu, and Co) located in a nitrogen-doped carbon matrix was demonstrated. Extensive characterization of these non-precious metal catalysts revealed important insights into the oxidation mechanism and stability of this new class of atomically-dispersed metal catalyst.



Biography

Robert Davis obtained his Ph.D. degree in Chemical Engineering from Stanford University in 1989. He subsequently worked as a postdoctoral research fellow in the Chemistry Department at the University of Namur in Belgium. He joined the faculty in Chemical Engineering at the University of Virginia in 1990 and is currently the Earnest Jackson Oglesby Professor. Professor Davis also served as the Chair of Chemical Engineering at the University of Virginia from 2002 to 2011. He received the Wilhelm Award of the AIChE, the Emmett Award of the North American Catalysis Society, the NSF Young Investigator Award, the DuPont Young Professor Award, the Union Carbide Innovation Recognition Award, and the UVA Rodman Scholars Award for Excellence in Teaching.



Using Catalysts to Create Differentiated Performance in the Production of Chemicals

Victor Johnston
Celanese Corporation

Celanese is a global technology and specialty materials company that engineers and manufactures a wide variety of products essential to everyday living. Catalysis is at the core of many of these technologies and materials, and the company has a long history of developing, improving, selecting, and using catalysts to make our processes and products better. However, while the focus of our business - what our customers wants, is often created by catalysis, that focus is rarely the catalyst itself. At Celanese we choose particular catalysts based on how they will function in our production units, and the role of the catalyst scientist at Celanese is to help ensure the best catalysts are deployed and used correctly. Sometimes that means developing new technology, and sometimes it means selecting from commercially available options. It always means learning how to translate from short-term microscale tests to long-term macroscale performance, and to drive improvements in an asymmetrical environment where the cost of failure can be larger than the potential benefit, but where driving improvement is imperative. These constraints push us to focus not only on the main catalyst features and reaction pathways, but also on how variations in those features, because of production variability, scale effects, operational constraints, environmental influences, and time on stream influence catalyst selection.



Biography

Victor Johnston is a Fellow in the Technology & Innovation organization at Celanese, located at the Clear Lake Technical Center in Pasadena, TX. He received his Bachelor of Science degree in Chemistry from Central Washington University in 1985 (shortly after Defense Secretary James "Mad Dog" Mattis), and a Ph.D. degree in Inorganic Chemistry from Simon Fraser University, Burnaby, BC Canada in 1989. After a post-doctoral fellowship at Indiana University, he joined the Intermediates and Catalysts R&D group of B.F. Goodrich in Brecksville, OH focusing on the development, testing and characterization of fluid bed catalysts. Following a spin off as The Geon Company and subsequent relocation to Texas in 1996, he spent several years supporting manufacturing, technology transfer, licensing, and catalyst sales efforts in the vinyl chloride monomer operations of the Geon Company (now a part of OxyVinyls, LP). Dr. Johnston joined Celanese in 2003 where he has had a variety of individual contributor and leadership roles. The varied geography brought with it a wide variety of chemistry, from beautifully useless tetranuclear osmium carbonyls to practical and profitable catalyst deployment optimizations. This work, thanks in large part to the contributions of many collaborators has resulted in 18 technical publications, over 150 US Patents, and led to honors including being named the 2013 Inventor of the Year by the State Bar of Texas. He is a member of the North American and Southwest Catalysis Societies, the American Chemical Society, and the Friendswood Drinking Club.

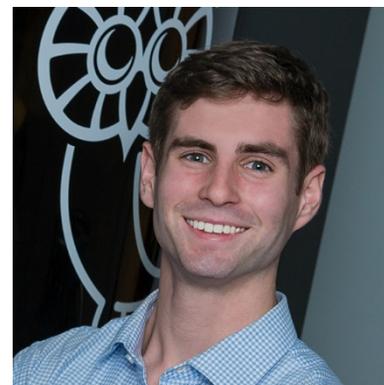


Student Presentation: Plasmon-mediated Catalysis with Aluminum-based Nanomaterials and Detection with THz Rotational Spectroscopy

Dayne F. Swearer

Rice University, Department of Chemistry

Catalysis is central to the modern world and contributes trillions to the global GDP. Despite the numerous advances in chemistry and engineering, combustion of fossil fuels is still the main energy source for the chemical industry today. As the world makes the transition to alternative forms of energy, the study and integration of alternative renewable energy sources, such as solar, is poised to help offset the tremendous costs, energy demands, and environmental pollution of the global chemical industry.



The research presented here seeks to understand the fundamental science of chemical reactions driven by light. On the nanoscale, certain varieties of metallic materials will show a collective oscillation of their conduction electrons, also known as a localized surface plasmon resonances (LSPR). Over the past two decades, the most commonly studied plasmonic materials were silver and gold, which, generally, are chemically inert and would be prohibitively expensive for large-scale adoption. Here, aluminum nanocrystals (AINCs) are introduced as an earth abundant material to perform catalysis directly on the intrinsic aluminum oxide layer and as an optical antenna to enhance light-driven chemistry on traditional transition metal nanoparticles. For example, plasmon-mediated catalysis with Al-Pd shows an increase in reaction selectivity under increasing light intensity for acetylene hydrogenation, leading to a 40:1 production of ethylene to ethane under illumination.¹ This effect is a result of the unique role that light-enhanced catalysis can have on these multicomponent systems. Furthermore, a general synthetic method has been developed to extend the catalytic library of these decorated AINCs to eight synthetic varieties, which will be the subject of future studies.²

In addition to discussing the fundamentals of light-driven catalysis on Al-based nanomaterials, frequency modulated terahertz (THz) rotational spectroscopy will be introduced as a new *in situ* method for monitoring gas phase reactants and products during chemical reactions.³ Exploiting its unambiguous molecular recognition specificity and extraordinary detection sensitivity, rotational spectroscopy at THz frequencies was used to monitor the decomposition of carbonyl sulfide (OCS) over an AINC plasmonic photocatalyst. The intrinsic surface oxide on AINCs is discovered to have a large number of strongly basic sites that are effective for mediating OCS decomposition. Spectroscopic monitoring revealed two different photothermal decomposition pathways for OCS, depending on the absence or presence of H₂O. The strength of rotational spectroscopy is witnessed through its ability to detect and distinguish isotopologues of the same mass from an unlabeled OCS precursor at concentrations <1 nanomole or partial pressures <10 μ Torr. These attributes demonstrate rotational spectroscopy as a compelling alternative for *in situ* monitoring of gas-phase chemical reactants and products in real time.

1. Swearer, D.F., *et al.*; *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113* (32), 8916

2. Swearer, D.F., *et al.*; *ACS Nano*, **2017**, *11* (10), 10281

3. Swearer, D.F., *et al.*; *Submitted*. **2018**.



POSTER ABSTRACTS

1. De-convoluting the Effects of Zeolite Framework Topology and Diffusion Path Length on Methanol-to-Hydrocarbon Reactions

Yufeng Shen¹, Thuy T. Le¹, Donglong Fu², Joel E. Schmidt², Bert M. Weckhuysen², and Jeffrey D. Rimer^{1*}

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For zeolite catalysts, the selection of crystal topology (i.e., network of pores) and the determination of crystal size (i.e., internal diffusion path length of pores) can affect catalyst performance;¹⁻² however, deciphering the relative impact of each factor on catalyst performance is often nontrivial owing to the inability to synthesize zeolites with predetermined physicochemical properties. In this study, a series of HZSM-11 (MEL) and HZSM-5 (MFI) catalysts of equivalent acidity, but differing pore architecture, are prepared with well-defined sizes to elucidate the effects of diffusion path length and topology on catalyst lifetime and selectivity. For these studies, we selected methanol to hydrocarbons (MTH) as a model reaction to assess the impact of these design variables on the hydrocarbon pool (HCP). *In situ* UV-Vis spectroscopy is used to investigate the evolution of active HCP species and heavier aromatic coking species over both sets of catalysts. Our findings reveal that slight variations in framework topology between MEL- and MFI-type zeolites results in marked differences of their catalytic performance as well as the evolutionary behavior of hydrocarbon species within the zeolite pores. We report that the diffusion limitation imposed by the tortuous channels in HZSM-5 catalysts is analogous to increasing the channel length in HZSM-11 catalysts, in that similar (albeit slightly offset) trends in MTH selectivity and catalyst lifetime are observed for both zeolites. However, we observe that differences in framework topology and catalyst size exact different effects on the evolution of intra-crystalline hydrocarbon species. We also show that the combination of catalyst synthesis, MTH testing, and *in situ* characterization provide compelling evidence that HZSM-11 is a high performance medium-sized pore zeolite catalyst for reactions where rapid coking is commonly prohibitive.

(1) Bleken et al., *Phys. Chem. Chem. Phys.* **2011**, *13* (7), 2539-2549.

(2) Khare, R.; Millar, D.; Bhan, A., *J. Catal.* **2015**, *321* (0), 23-31.



2. The Marriage of Activity and Selectivity in the Oxidative and Non-Oxidative Activation of Methane on Gold-Palladium Alloys

Quan K. Do, Hung Tran-Vu, Shengguang Wang, and Lars C. Grabow*

Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204

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The grandest challenge in the direct upgrade of methane to useful chemicals is finding a catalyst that is active for the difficult C-H bond scission, yet selective such that not all of the C-H bonds break to form coke. These requirements inevitably lead to the downfall of single metals, including palladium and gold. Palladium is highly active for the C-H bond scission of methane, but the dehydrogenation is carried out to completion, indicating poor selectivity. Meanwhile, gold is selective for methane activation because the methyl adsorbate would rather desorb than dehydrogenate further, but breaking the initial C-H bond of the inert methane molecule is a great obstacle, which illustrates the catalyst's poor activity.

To maximize the strengths and minimize the weaknesses of the gold and palladium single metals, we combined the metals to form a binary alloy; gold-palladium alloys have been used previously for the selective oxidation of methane to methanol.¹ Further motivated by the unique surface properties of single atom alloys,² where one highly active promoter atom sits within the surface of a less reactive host atom, we selected the Au₃Pd alloy, where every surface Pd atom is fully surrounded by Au atoms. Using density functional theory, we compared the pathways and mechanisms of non-oxidative and oxidative methane activation on Au₃Pd(111) with the monometallic Pd(111) and Au(111) systems. In the non-oxidative mechanism, the inclusion of small quantities of Pd in Au drastically decreases the activation energy for the activation of methane, yet the formed methyl remains more likely to desorb than to further dehydrogenate, representing the unison of catalytic activity and selectivity. In the oxidative mechanisms, we elucidated the interaction of methane with pre-adsorbed O*, OH*, O₂*, and OOH*, and determined that the true role of Pd on the Au₃Pd(111) surface is to draw oxygen species to the noble Au surface, which is highly active if oxygen-based adsorbates are present. Since the oxygen adsorbates occupy the Pd atom, the product methyl adsorbate must bind to the Au sites, where it is selective to further chemistry. Thus, we find that the Au₃Pd alloy constitutes an ideal marriage of activity and selectivity for both the non-oxidative and oxidative activations of methane.

- (1) Rahim, M. H. A.; Murphy, D. M.; Kiely, C. J.; Hutchings, G. J.; *Angew. Chem. Int. Ed.* 52 (2013) 1280-1284.
- (2) Kyriakou, G.; Boucher, M. B.; Jewell, A.D.; Lewis, E.A.; Lawton, T.J.; et al.; *Science*. 335 (2012) 1209-1212.
- (3) Yoo, J. S.; Khan, T. S.; Abild-Pedersen, F.; Nørskov, J. K.; Studt, F.; *ChemComm*. 13 (2015) 2621-2624.



3. Effect of pretreatment on Lanthanum Zirconate pyrochlore catalyst in Dry reforming of Methane

Srikar Bhattar¹, Aiswarya Krishnakumar², Swarom Kanitkar¹, Ashraf Abedin¹, Dushyant Shekhawat³, Daniel J. Haynes³ and James J. Spivey^{1*}

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Dry reforming of Methane is one of the promising methods to produce syngas. Temperatures approaching 900°C are needed to reach equilibrium so thermally stable catalysts are required. Ni catalysts are widely studied for DRM, but are prone to coking and sintering¹. Thermally stable Lanthanum Zirconate Pyrochlores (La₂Zr₂O₇) were selected for our current work. Modified Pechini method was used to produce the catalyst (LSNZ6, 6wt% Ni), in which the La site is partially doped with Sr while the Zr site with Ni. Catalyst was analyzed with thermal and spectroscopic characterization techniques for DRM to study the effect of pretreatment—oxygen or hydrogen. Effect of pretreatment on the catalyst was observed by performing 45hr runs of DRM. The fresh calcined catalyst showed the expected pyrochlore structure using XRD. In addition, a perovskite phase of Ni and NiO phase were also identified. Perovskite phase was also seen by Haynes et al.². A small quantity of Ni appears to substitute the pyrochlore structure based on the change of the lattice constant. XPS and SEM-EDS analysis confirmed that Ni is substituted more into the bulk perovskite and pyrochlore phases than on the surface. TPR showed the presence of two major reduction peaks at different temperatures, indicating the presence of different dispersion of Ni. TPSR showed that the catalyst is active above temperatures of 750°C. There was no evidence of carbon deposition from the post reaction TPO. From the 45hr DRM runs at 900°C, the type of pretreatment significantly affects the time needed to reach equilibrium conversion. The catalyst sample pretreated with 10%O₂/He showed equilibrium conversion within several minutes (around 30min), while the sample pretreated with 10%H₂/Ar reached equilibrium only after 20hr, indicating that both catalysts reached equilibrium at these conditions, but far more rapidly for the catalyst pretreated with oxygen. A study by Gallego et al.³ on DRM using a LaNiO₃ perovskite showed that equilibrium was reached far more rapidly for the catalyst that was oxidized in their synthesis process than the catalyst pretreated using hydrogen.

(1) Araujo, G. C. d.; Lima, S. M. d.; Assaf, J. M.; Pena M. A.; Fierro, J. L. G.; do Carmo Rangel, M.; *Catal. Today* 133-135 (2008) 129-135.

(2) Haynes, D. J.; Shekhawat, D.; Berry, D. A.; Zondlo, J.; Roy, A.; Spivey, J. J.; *Ceramics International* 43 (2017) 16744-16752.

(3) Gallego et al., *Applied Catalysis A: General* 311(2006) 164-171.



4. Recyclable In-Pd bimetallic catalysts for nitrate reduction

Sujin Guo^{1,2}, Kimberly N.Heck^{2,3}, Camilah Powell^{2,3} and Michael S. Wong^{1,2,3,4,5*}

¹Department of Civil & Environmental Engineering, ²Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment, ³Department of Chemical and Biomolecular Engineering, Rice University, 6100 S. Main Street, Houston, TX 77005, ⁴Department of Chemistry, ⁵Department of Materials Science and NanoEngineering, Rice University, 6100 S. Main Street, Houston, TX 77005

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Nitrate (NO₃⁻) is an ubiquitous groundwater contaminant, and is detrimental to human health. Bimetallic palladium-based catalysts have been found to be promising for treating nitrate (and nitrite, NO₂⁻) contaminated waters. 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. Indium speeds up the breakdown of nitrates while the palladium apparently keeps the indium from being permanently oxidized. This improved understanding of the In active site expands the prospects of improved denitrification using metal-on-metal catalysts. After big achievements in understanding the mechanism, we deposited the In-on-Pd NPs on the Fe₃O₄ magnetic core in order to easily recycle the catalysts after each reaction and increase the possibility in future scale up design. The magnetic In-Pd catalysts show high chemical stability and recyclability during cycle experiments. This is going to be an example within Nano-enabled Water Treatment (NEWT) Center where we have the chemistry figured out, and the next step is to create a flow system to show proof of concept that the technology can be used in the field.



5. Optimizing ZSM-11 Synthesis using 1,8 – Diaminooctane as a Structure-Directing Agent

Thuy Le, Yufeng Shen, and Jeffrey Rimer*

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ZSM-11 (MEL framework) is a zeolite catalyst with potential in a wide range of catalytic applications. The structure of ZSM-11 is closely related to ZSM-5 (MFI framework), which is a well-known industrial catalyst; however, ZSM-11 has straight channels compared to more tortuous ones of its counterpart. This factor is posited to be one of the key reasons for the reduced diffusion limitations in ZSM-11 and its improved catalyst lifetime compared to ZSM-5;¹⁻³ yet there are relatively few published studies of ZSM-11 synthesis, which may be related to several difficulties associating with synthesizing pure, submicron crystals with inexpensive organic structure-directing agents (OSDAs). Here, we examine ZSM-11 synthesis using a relatively inexpensive and commercially available OSDA, 1,8-diaminooctane (DAO). In combination with parametric studies and seeded synthesis, we successfully prepared ca. 300nm ZSM-11 crystals with excellent yield (> 80%) via a commercially viable process. Furthermore, benchmark methanol to hydrocarbon (MTH) reaction testing reveals a comparable catalytic performance (i.e. lifetime and selectivity) for samples prepared with and without seeds.⁴ We observe a morphological difference from synthesis with two different types of MEL seeds and more notably, a zeolite phase transition between two frameworks (MEL and TON), which is interesting given the fact that these crystals do not share a common building unit (as has been recently predicted for intercrystalline zeolite transformations in the literature⁵). In summary, our findings underline an efficient method to produce ZSM-11, which is a promising alternative to common industrial catalysts such as ZSM-5. Through systematic analysis of synthesis parameters, we observe unique aspects of zeolite polymorph control and methods to optimize the physicochemical properties of ZSM-11 materials.

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6. Enhancement of Mo/H-ZSM5 catalysts in methane aromatization by addition of Fe promoters and by reduction/carburization pretreatment

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Due to a substantial decline in the world petroleum reserves, increase in oil prices and growing global demand, effective utilization of natural gas has become extremely important. Methane, being the major component of the natural gas, is widely recognized as a potential alternative fuel source that can be used to produce important chemicals. Since Wang et al.¹ reported the first efficient catalyst in 1993 for non-oxidative methane aromatization, which converts methane to aromatic compounds and hydrogen, using MoO_x supported on ZSM-5 as catalyst, extensive investigation has been carried out on zeolite-supported molybdenum oxide catalysts in the past few decades. However, detrimental coke formation which causes relatively fast deactivation of the catalysts is a major hindrance towards commercialization of the catalyst. Therefore, it remains an ambition for the chemical industry to develop a process to upgrade natural gas to useful aromatics that is economically viable.

Our work involves investigating ways to impede deactivation by carbonaceous deposits by studying the effects of doping Mo/ZSM5 catalyst with Fe and using different pretreatments, namely heating the catalyst under He flow and carburizing in CH₄ after reducing in H₂/CH₄. Structural characterization and the activity results show that pre-carburized catalysts are more stable due to the formation of smaller amounts of carbon deposits, and consequently lower pore blockage. Addition of Fe causes the carbon deposits to be more reactive and easier to burn off. Higher Fe loadings are linked to the formation of carbon nanotubes.

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7. Multifunctional Materials for Catalysis: Supported Dendron Encapsulated Palladium Nanoparticles

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Dendrimer-encapsulated nanoparticles (DENs) have attracted interest since they were first introduced. This synthetic approach leads to well-defined sizes, compositions and structures of nanoparticles controlled by the dendrimer template [1]. In previous work, melamine-based dendrimers were successfully grafted to OMS supports through the bridge of organosilanes [2]. More recently we have used the supported dendrimer hybrid materials as templates to form small and uniform palladium nanoparticles [3]. Multiple characterizations were used to validate both the structural integrity of the dendrimers and the nature of the metal nanoparticles formed. Probe reactions have showed the accessibility of both metal sites and amine sites from dendron.

Here, these supported dendron encapsulated palladium hybrid materials were used as multifunctional catalysts in a two-step catalysis scheme in water: 1) phenol hydrogenation and 2) aldol condensation. Preliminary results show that a phenol conversion of 95% with 99% selectivity to cyclohexanone can be obtained using these hybrid materials as catalysts in 3 h under mild conditions (50 °C, 15 psi H₂). Additionally, the supported dendrimer hybrids were active in aldol condensation of cyclohexanone and nitrobenzaldehyde in the presence of water with different syn/anti product selectivity. Such multifunctional materials should be of broad interest to the materials community for a range of engineering problems.

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8. “Tunable Activity in the Selective Catalytic Reduction of NO_x by Varying Synthesis Conditions of Zeolite SSZ-39”

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The work presented here explores how the synthesis conditions of zeolite SSZ-39 propagate into the catalytic activity of the selective catalytic reduction (SCR) of NO_x. SSZ-39, the aluminosilicate analogue of the AEI (AlPO₄-18) topology, can be prepared in a straightforward manner using faujasite as an aluminum source. A variety of organic SDAs have been shown to afford SSZ-39 at various levels of efficacy, including N,N-dimethyl-3,5-dimethylpiperidinium, the organic SDA employed here. We have previously reported that the cis/trans ratio of the SDA will influence the Si/Al ratio of the resulting zeolite. The Si/Al of the gel also influences the resulting Si/Al of the zeolite product. Following copper ion-exchange, SSZ-39 catalysts are tested across synthesis conditions by varying the Si/Al of the gel as well as the makeup of the SDA isomer. The NO conversion is presented on both a per gram of catalyst basis as well as a per mol of copper basis across temperatures ranging from 150 to 550 °C.



9. Transition metal-doped rare-earth oxysulfide catalysts for high temperature dry reforming of methane

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The purpose of this work is 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., Ni/Ce-Zr) systems that can be tolerant of sulfur and water at realistic levels, an extension of our previous work on tar reforming. To date, we have tested different many different metal/REO combinations (Ni, Mn, Co, Fe, Pd, Ru, W)-doped Ce/La and Ce/Zr catalysts at 725-775°C for dry reforming (1:1 CH₄:CO₂) and combined dry/steam reforming (1:1 CH₄:CO₂ but with water added). Many of these tests were performed using a TGA/DSC method we developed to simultaneously and rapidly measure dry reforming and coking rates. Ni- and Ni/Co-doped catalysts are the only suitable combinations, with Ce/Zr. All other catalysts are either relatively inactive, or unstable under dry reforming conditions, or coke too fast, or catalyze too much reverse water-gas shift. While some of the better catalysts are stable in feeds of 0.07 ppm S, none so far are stable in 20 ppm S, although work is continuing. Used catalysts have to date been characterized by Raman spectroscopy, XRD and CO chemisorption.



10. Identity and State of Extraframework Species in Metal Exchanged Zeolites – Simulation of Characterization Spectra using Molecular Simulations and Theory

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Zeolite catalysts are extensively used in petroleum refining, and metal exchanged zeolites are known to be active in processes such as hydrocarbon upgrade.¹ Metal species are exchanged into zeolites as cations to charge balance acid sites present in the zeolite. This results in a strong localized electric field or a Lewis acidity in conjunction with the shape selectivity offered by the zeolite pores. A combination of these factors often manifests itself into catalytic behavior, especially in reactions such as methanol to olefins.² While a lot of knowledge has been gained from detailed experimental and computational investigations into the catalytic activity of metal exchanged zeolites, the understanding of the state of the metal active sites within the zeolite pores is less certain. Researchers often make use of findings from characterization studies, along with some simplifying assumptions to arrive at computational models.

With the advancement of underlying theory and computational power, it is now more feasible to recreate spectra typically used to characterize metal exchanged zeolites providing a means to justify and validate the use of computational models. In this work, we attempt to recreate some commonly used techniques in the field of metal exchanged zeolites i.e. UV-vis spectroscopy, X-Ray Absorption Spectroscopy (XANES and EXAFS) and X-Ray Photoelectron Spectroscopy (XPS) specifically for Ag exchanged ZSM-5. We obtain good agreement between the experimental spectra and simulated spectra, confirming that a computational model with a single Ag⁺ cation charge-balancing an acid site is indeed the active site in Ag exchanged ZSM-5.³

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11. Support Effects for the Selective Hydrogenation of 1-Octyne on Au/MO_x

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Polyolefin feedstocks such as ethylene, propylene, and butene typically contain ~2-10% alkyne impurities. Downstream polymerization catalysts are poisoned by these impurities, so it is vital to decrease their concentration as low as 10 ppm.¹ Industry currently uses Pd catalysts to selectively convert alkynes into olefins. However, Pd itself has several disadvantages: over-hydrogenation of alkynes into alkanes, conversion of the majority-olefin feed into alkanes, and deactivation through the formation of oligomers (“green oil”). Gold catalysts are an attractive alternative to Pd due to weak ethylene binding. Previous studies involving Au found superior olefin selectivity when compared to Pd, but Au required prohibitively high process temperatures (> 200 °C).^{2,3} Relatively little is understood about the fundamental hydrogenation chemistry on Au and the factors that improve catalytic activity. The goal of this study was to quantify how different supports affected the Au nanoparticle for selective hydrogenation.

Supported Au catalysts were synthesized through a colloidal method. MO_x supports included Al₂O₃, TiO₂, SiO₂, and Fe₂O₃. The adsorption of 1-octyne, an analog for acetylene, was observed via FTIR for selected catalysts. Initial activity was measured with lightoff curves for the hydrogenation of 1-octyne, and kinetic parameters were also determined (E_{app} , 1-octyne order, H₂ order). Surprisingly, the results for all of the catalysts were nearly identical, suggesting that the electronic effects from the support to the Au nanoparticle were negligible. The rate is likely determined by H₂ activation (~1st order), so the lack of a significant support effect indicates that the reaction occurs on low-coordinated Au sites on the Au nanoparticle, not the Au-MO_x interface.⁴ Minor differences in overall rate could be explained by the quantity of active sites via Michaelis-Menten characterization.

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12. Mechanistic Implications from the Detection of Hydrazine in the Aqueous-Phase Reduction of Nitrite over Precious Metal Catalysts

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Nitrate (NO_3^-) and nitrite (NO_2^-) are among the most common groundwater and surface water contaminants arising from the increased use of nitrogen-rich agricultural fertilizers. These oxyanions have severe health effects on both humans and aquatic life. Many remediation technologies have been investigated, including those based on catalytic reduction. Pd-based catalysts have been the most studied for this reaction where a promoter metal (In, Cu, Sn) is needed to catalyze the initial reduction of nitrate to nitrite. These catalysts typically demonstrate high nitrate/nitrite reduction activity with selectivity primarily to dinitrogen over ammonium (NH_4^+). Other noble metals have been less studied for this reaction because of their higher selectivities towards NH_4^+ ; however, these alternative metals can exhibit a variable pH dependence compared to Pd and expand the scope of operating conditions for denitrification.

In this work, we studied the room-temperature reduction of NO_2^- over monometallic Pd and Rh supported on alumina. Here, Rh was found to have a pH dependence opposite of Pd catalysts, which show high activity under acidic conditions and decreasing activity with increasing pH. Over the Rh catalyst, we observed a remarkable (>90%) selectivity to ammonium at all pH values. We also report the direct observation of hydrazine (N_2H_4) reaction intermediate, which has previously only been a proposed intermediate. Experimental observations and density functional theory (DFT) simulations together suggest that (1) the adsorbed NO species is the primary intermediate which determines the selectivity towards N_2/NH_4^+ and (2) N_2H_4 formation most likely proceeds through the coupling of adsorbed NH_2 species. This study highlights and accentuates the reactivity differences between Rh and Pd, which are primarily due to the ability of each metal to dissociate adsorbed NO species. The quantification of hydrazine in the bulk also suggests chemistry which can lead to the synthesis of other useful N-containing compounds. Our findings indicate that nitrite reduction over supported Rh-based catalysts shows promise as a strategy for the sustainable regeneration of ammonium compounds at low temperature and pressure from nitrate- and nitrite-rich waste streams and also provide a valuable supplement to the mechanistic understanding of catalytic denitrification.



13. Mechanistic investigation of partial oxidation of methane to methanol using O₂/H₂O mixtures

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Methane is the primary component of shale gas and has attracted renewed attention to its potential direct conversion into value-added products such as methanol. The currently used two-stage process of steam reforming to synthesis gas, followed by methanol production from synthesis gas is only profitable at very large scale considering the high energy and infrastructure requirements. In contrast, single step conversion of methane to methanol is attractive for distributed processing and yields a liquid product directly. However, the selective activation of C-H bonds in methane is a challenging task because of the strong C-H bonds demanding high reaction temperatures, which, in turn, result in complete oxidation decreasing selectivity.¹ These pervasive challenges in oxidative upgrade of methane make it an interesting topic for high-impact scientific research with the single step conversion of methane to methanol often referred to as the “Holy Grail of Catalysis”.²

Hydrogenperoxide was shown to partially oxidize methane to methanol through OOH* and OH* intermediates.³ Under the right conditions, mixtures of O₂, and H₂O also form reaction intermediates OOH* and OH* at the Au/TiO₂ interface.⁴ Both reactants are safe and inexpensive, particularly when compared to the alternative route from hydrogenperoxide, making the oxidation more viable for small and large scale industrial processes. We present the comprehensive density functional theory study of the mechanistic pathway for oxidation of methane to methanol by O₂/H₂O mixtures on Au/TiO₂. We explore the activation of O₂ to OOH* and OH* by water at Au/TiO₂ interface in this study. The barrier for the rate limiting step of initial C-H activation was found to be lower with OH* group than the other sites, proving the effectiveness of O₂/H₂O mixtures as oxidants for methane.

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14. Oscillations and Hysteresis during Hydrocarbon Oxidation on a Diesel Oxidation Catalyst

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The impact of zeolite beta (BEA) was studied during hydrocarbon oxidation on a diesel oxidation catalyst (DOC). The oscillatory CO₂ formation was measured under steady-state and transient-feed by the spatio-temporal techniques of spatially-resolved mass spectrometry (SpaciMS) and coherent optical frequency domain reflectometry (c-OFDR) [1]. The oscillatory CO₂ formation leads to significant local temperature rise, which may deactivate the catalyst. The coupling between hydrocarbon sorption and oxidation is proposed to be the mechanism for the oscillatory CO₂ formation. A monolith reactor model was developed to simulate the hydrocarbon adsorption and reaction during the dodecane oxidation to enhance the understanding of the mechanism of the oscillatory CO₂ formation on the BEA/DOC catalyst. A series of steady-state experiments were conducted to determine the kinetic parameters of the dodecane oxidation and sorption. The model and data show a good agreement in the oscillatory region. The model explains that the oscillatory behavior was caused by a tug-of-war between the oxidation and sorption, verifying the experimental results. Experiments determined the impact of the average fluid velocity on the oscillatory occurrence. A non-dimensional zed map was constructed to guide the prediction of the conditions leading to the oscillatory occurrence. A beneficial effect of the wider hysteresis behavior was observed experimentally and theoretically in coupling of the hydrocarbon sorption and oxidation, decreasing the hydrocarbon emission. Experimental measurements of temperature hysteresis between the ignition and extinction were compared with modeling predictions under various fluid velocities and feed-concentrations. The modeling predictions closely matched the experimental results, suggesting that the developed model may be used to predict the oscillatory CO₂ formation conditions and dynamic hysteresis width.

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15. Synthesis of Steam-Assisted Crystallized Fe-ZSM-5 Materials and Their Exceptional Application in Benzene Hydroxylation to Phenol

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The direct synthesis of phenol from benzene has been identified as one of the ten most demanding transformations in the petrochemical industry. Phenol is currently made via the cumene process where acetone and phenol are formed in a 1:1 ratio. Due to the challenges in utilizing molecular oxygen and nitrous oxide as oxidants, the development of a liquid-phase direct oxidation of benzene using hydrogen peroxide as an oxidant stands as an alternative one-step route^[1]. Obtaining a high selectivity to phenol is a critical parameter for the evaluation and utilization of catalyst for this reaction. While numerous Ti-based materials have been studied for benzene oxidation in the liquid phase including Ti-MCM-41, Ti-Beta and Ti-SBA-15^[2-4], MFI-type zeolites have been the focus of significant research in benzene oxidation catalysis owing to the fact that the pore size of the MFI lattice is comparable to the diameter of the benzene molecule and may impart high phenol selectivity.

A series of Fe-ZSM-5 samples with steam-assisted crystallization (SAC) and conventional methods were successfully synthesized. All the characterizations (XRD, FE-SEM, UV-Vis, In-Situ IR, etc.) related to these materials are presented. It has been shown that due to much less diffusion resistance and enhanced H₂O₂ activation, the mesoporous samples show superior performance over the microporous Fe-ZSM-5 materials in benzene oxidation at mild conditions. The best synthesized sample gives conversion of 25.5% with phenol selectivity of 90% after 8 hours. In the same conditions, TS-1 catalyst indicates 1.1 % benzene conversion and 63% phenol selectivity. These encouraging results show SAC samples have potential to be used as solid catalysts in benzene oxidation.

Keywords: Cumene Process, Steam-Assisted Crystallization, Mesoporous Fe-ZSM-5, Benzene Oxidation, Phenol.

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16. Copper-Gold Nanoparticles Encapsulated Within Surface-Tethered Dendrons as Supported Catalysts for the Click Reaction

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This paper will present our recent work on the synthesis, characterization, catalytic testing and operando IR of CuAu nanoparticles formed in melamine dendrons grown off SBA-15. Given our initial inability to form copper nanoparticles that were resistant to rapid oxidation, we decided to form copper overlayers on gold nanoparticles that were formed in the dendrons. We will show results including STEM, UV-Vis, and XPS that confirm that the copper overlayers deposited on gold are stable Copper(0) in nature.

After briefly showing how the dendron identity influences the particles sizes of the metals obtained, the talk will focus on the catalytic efficacy of the materials for the click reaction. Controls show that copper is needed to perform the reaction. How the copper:gold ratio, dendron generation, and metal loading impact the catalytic rates observed will be described. In our hands a copper:gold ratio of 1:3 appears to be an optimum, resulting in high atom utilization of the copper. In this case we see near quantitative conversion at 323 K in 15 hours. To probe whether the observed reactivity is due to modulation of the electronic properties of the copper or simply a result of high dispersion we employed operando IR spectroscopy to monitor the formation of products, intermediates, and consumption of reactants. Those studies clearly demonstrate that our synthesis methodology leads to higher copper utilization, as we do not observed selective enhancement of individual steps in the reaction pathway, but rather simply an increase in the rate of what appears to be all steps in the mechanism.

The talk will conclude with a brief discussion of the stability of these materials as determined by recycle studies and the role of metal leaching and how that varies in the mixed metal system and the presence and absence of the dendron.



17. Acetic Acid Extraction Using Amine Grafted OMS: Effects Due to Degree of Amine Methylation

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Cellulosic biomass represents a potential feedstock for the production of sustainable fuels, but currently requires a large energy input to be depolymerized into sugars suitable for enzymatic digestion. Organic acid side products, with the majority being acetic acid, produced during depolymerization of cellulose are a large energy sink for the process because they must be selectively removed in order to raise the pH to a range that enzymes can efficiently produce alcohols. Liquid amine sorbents have been traditionally used for this due to their inherent basicity, but suffer from a large energy penalty during separation. Additionally, the nature of the extraction is not fully understood with many competing molecular forces at play. By grafting amine functional groups on the surface of a high-surface area support, the separation could be significantly less energy intensive while maintaining high uptake and be used as a model substrate to provide a better mechanistic understanding of the extraction process.

In this work, amine grafted ordered mesoporous silica (OMS) was used to extract acetic acid and the acid uptake of primary, secondary, tertiary, and quaternary methylated amines were compared. By changing the degree of methylation on the amine ligand, the charge on the ligand is varied resulting in different extraction properties. The amine grafted OMS materials were also tested for extraction at various pH, salt concentrations, and in the presence of realistic sugar concentrations to provide mechanistic insights as well as test their viability in an industrial process. Additionally, organic acids with different hydrophobicity's were tested for uptake and competing uptake to compare amine selectivity. The obtained results reveal the best ligand for specific applications as well as a path to synthesize high ligand loaded materials for large amounts of selective organic acid extraction.

These results can also provide valuable insight into not only organic acid extraction, but could also be applied to other applications where acid-base interactions are involved. For example, it is hypothesized that amine-metal ion chelation and amine supported catalysis could be significantly affected by the degree of amine methylation based on these results.



18. Effect of temperature for sulfated Hafnia supported Mo₂C catalyst in methane dehydroaromatization

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One of the most challenging aspects of modern day catalysis is the conversion of methane. Methane dehydroaromatization (MDHA) is a direct conversion process of methane to produce hydrogen and valuable hydrocarbons like benzene. Mo oxide supported on ZSM-5/MCM-22 has been studied extensively in recent years for MDHA. It has been reported that Mo carbides are responsible for activating methane by forming CH_x species. These are dimerized into C₂H_y and later oligomerized on the acidic sites available on ZSM-5/MCM-22 support.¹ Previously in our lab, sulfated Zirconia showed high benzene selectivity as an acidic support for Mo in MDHA. As a continuation of that study, sulfated Hafnia (SH) replaced the conventional ZSM-5 as a support for Mo. The goal was to study the acidity of SH as a function of temperature for MDHA. 5 wt. % of Mo was loaded on SH by incipient wetness impregnation. DRIFTS was run to characterize the surface acidity using the FT-IR spectra of chemisorbed pyridine.

In situ catalytic pretreatment was carried out using Hydrogen to reduce the catalyst till it reached the desired reaction temperature, i.e., 600°C, 650°C and 700°C. Subsequently 1:4 flow of CH₄:H₂ was used to form the active Mo₂C phase. Products observed in the three reaction runs include Ethylene, Ethane, Propylene, Propane and aromatics (Benzene, Toluene, Xylene etc.), as well as significant amount of Hydrogen. Methane conversion increased with temperature. Activity decreased significantly over time at higher temperature, likely due to coking². This was confirmed with subsequent TPO.

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19. Heavy Oil Viscosity Reduction Using Iron(III) Tosylate Hexahydrate —A Kinetic and Temperature-Dependent Study

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Heavy oil is an abundant energy resource but its production remains challenging primarily due to its high viscosity. Thermally enhanced oil recovery in the presence of metal-ligand compounds represents a promising method for viscosity reduction. While catalytic chemistry has been proposed to be responsible for effective viscosity reduction, the interactions between metal-ligand compounds and crude oil components at the molecular-level are poorly understood and thus the mechanism remains unknown. Here, we studied heavy oil viscosity reduction in a range of 80 - 295 °C with or without iron(III) tosylate hexahydrate ($\text{Fe}(\text{pts})_3 \cdot 6\text{H}_2\text{O}$), and analyzed the reaction products via viscometry, TGA-MS, UV-vis-NIR spectroscopy, GC-MS, SARA measurements, XRF and XPS. It was observed that iron complex increased oil viscosity below 220 °C but started to reduce viscosity at 250 °C, and TGA and UV-vis-NIR data also suggested a complete loss of one pts ligand occurred at 250 °C. These results implied that reaching an activation temperature is required for oil viscosity reduction. We also identified 4-methylbenzenethiol in the post-reaction oils ($\text{Fe}(\text{pts})_3 \cdot 6\text{H}_2\text{O}$ and ≥ 250 °C) by GC-MS, which is likely converted from the released pts ligand that acts as a deviscosifier. SARA analyses showed noticeable drop in resin fraction and XPS analyses showed the aliphatic sulfur content of resins was reduced after the reaction. Our findings revealed some aspects of the fundamental mechanisms of oil viscosity reduction using metal-ligand compounds. This work expands the knowledge of catalytic chemistry and will aid future designs of metal-ligand compounds for thermally enhanced oil recovery.



20. Dual Role of Surfactants towards a Rational Design of Zeolites

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Zeolites are crystalline microporous aluminosilicates with unique properties, such as tunable acidity and exceptional (hydro)thermal stability, which are utilized in commercial processes ranging from ion-exchange and adsorption to catalysis and separations. Surfactant templating has emerged as one of the most effective and versatile strategies for the construction of well-defined porous architectures in zeolites.¹ Despite tremendous effort to elucidate the mechanisms of surfactant templating in zeolite synthesis, these pathways are not well understood. Here, we will discuss the dual roles of the surfactant cetyltrimethylammonium (CTA) as a structure-directing agent (SDA) and mesostructuring agent in the design of zeolites.

One of the most common zeolites is ZSM-5 (MFI type), which is used as a catalyst and sorbent in a wide range of industrial applications. In ZSM-5 synthesis it is challenging to identify new and inexpensive organic SDAs that can tailor the physicochemical properties of the final product. The most frequently used SDA in ZSM-5 synthesis is tetrapropylammonium (TPA); however, recent studies have shown that CTA can be used as an alternative.^{2,3} Here, we will present the effects of dual structure-directing agents using CTA and TPA as organic SDAs in combination with a variety of alkali metals as inorganic SDAs. Our findings reveal that the selection of inorganic/organic SDA combinations has a significant impact on the kinetics of ZSM-5 crystallization, as well as the properties of the resulting crystals. Notably, we show that TPA/Na and CTA/K are optimal combinations of SDAs that can markedly alter the size, morphology, and aluminum distribution in ZSM-5. Using a combination of experiments and molecular modeling, we explore the use of CTA as an alternative organic SDA for zeolite MFI and show that we can achieve smaller crystals (ca. 600 nm) in similar time (< 24 h) as syntheses employing TPA.

In addition to SDA design, the development of mesoporosity in zeolites has been a long-standing goal in catalysis to alleviate the diffusion limitations imposed by micropores. One of the most exciting, yet not fully understood phenomenon, is the rearrangement of zeolite crystals to accommodate mesoporosity. Here, we will present *in situ* observations of intracrystalline mesoporosity in USY zeolite (FAU type) assisted by CTA using atomic force microscopy. Our findings capture in real time the structural, morphological, and textural evolution of initially rough crystals to smooth crystals with a uniform distribution of mesopores.

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21. Catalysis of the Diels-Alder Reaction of Furan and Methyl Acrylate in Lewis-acidic Zeolites

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Diels-Alder (DA) reactions of furans yield oxanorbornene derivatives which can be converted to a variety of molecules, ranging from molecules of biological interest to naturally occurring organic compounds, and to aromatics via dehydration, a promising alternative for the synthesis of aromatics from renewables. With furan being one of the less reactive dienes, development of Lewis-acidic heterogeneous catalysts, without the shortcomings of the traditional homogeneous ones, is critically important. Herein, we use computational chemistry to study the DA reaction of furan and methyl acrylate in three zeotypic Lewis acids, Sn-, Zr- and Hf-BEA. We find that all three exhibit the same ability to enhance the electrophilic character of the dienophile and promote modest charge transfer from the diene. Despite being moderately Lewis-acidic, they still achieve a reduction of about 12.5 kcal/mol in the activation energy relative to the thermal reaction.¹

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22. Computational Study of Carbonate Assisted Electrochemical Methane Activation on Ni(111) Using Density Functional Theory

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While being an abundant resource in the U.S., methane has very strong C-H bonds, which makes it energy consuming to be activated. Thus, the development of efficient catalysts to upgrade methane to higher value products is both, challenging and very desirable. Two major issues that current catalysts are facing are that high temperatures (up to 900K) are required, and the life time of the catalysts is limited due to sintering and coking. Inspired by the work of Spinner and Mustain¹ we aim to address these challenges and pursue a novel low temperature process, which leverages the use of an electrochemical cell to convert methane to methanol.

The envisioned process uses carbonate anions (CO_3^{2-}) that are produced from CO_2 and O_2 at the cathode and transferred to the anode through an electrolyte. At the anode, carbonate ions serve as activator for methane and the transfer of a single oxygen atom can selectively oxidize methane to methanol. The fact that carbonate anion reduction leads again to CO_2 , which readily desorbs into the gas phase, is considered a key advantage of the proposed electrochemical process. By simultaneously controlling the concentration of CH_4 at the anode and the rate of CO_3^{2-} delivery by adjusting the cell potential and current density, we anticipate that the over-oxidation of methane can be prevented, such that a high yield of methanol can be achieved.

To obtain fundamental insight into the feasibility of such process, we have performed density functional theory (DFT) calculations on Ni(111) in VASP and explicitly accounted for the effects of external electric fields. Our results show that the external electric field has less impact on the binding energy of nonpolar intermediates (CH_4 and CO_2) than that of polar intermediates (CH_3 , OH , CH_3OH , etc.). Hence, the reaction enthalpy and activation energy of certain elementary steps exhibit a strong dependence on the applied electric field. We have quantified the electric field effect for two distinct reaction pathways and postulate that a properly tuned electric field can guide the reaction to proceed in the desired direction. While the development of a viable process remains in its early stages, our results suggest that a tunable electric field in an electrochemical cell offers unique advantages for selectively upgrading methane to value-added products.

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23. Understanding the Role of H₂O in H₂ Activation on Metal Oxide Supported Au

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Hydrogen is an important reactant in a number of organic reactions (e.g. selective hydrogenation of acetylene and 1,3-butadiene) as well as inorganic applications like the Haber-Bosch process. Traditional hydrogenation metals like Pt, Pd and Ni, have very high activities, but suffer from poor selectivity. Au on the other hand offers intrinsically high selectivity but poor activity. The goal of this study is to investigate the hydrogen activation mechanism on Au, particularly the role of H₂O, in order to improve Au-based selective hydrogenations.

The bulk of the kinetic investigation was done using H₂ oxidation, which has specific relevance to the Preferential Oxidation of CO (PrOx) reaction. It has been previously established that H₂O plays a critical role in CO oxidation by activating O₂ on Au; [1] this promotion is also seen when H₂O coverage is controlled during PrOx [2]. In order to evaluate water's role in H₂ oxidation and activation, a thorough kinetic analysis was performed and supported by DFT calculations and a spectroscopic investigation.

Some key observations were made during the kinetic analysis of H₂ oxidation. Firstly, H₂ is approximately 1st order. This demonstrates a difference from CO in CO oxidation where CO is nominally 0th order, meaning H₂ activation is likely the rate determining step. Secondly, O₂ is weakly positive order, by the same magnitude as the O₂ order in CO oxidation. This suggests that in both CO and H₂ oxidation, the same O₂ reactive intermediate is generated and CO and H₂ compete for this species in PrOx. Lastly and importantly, H₂O was found to be strongly negative order for H₂ oxidation. H₂O is positive order in CO oxidation, so H₂O must play a different role in the catalysis of H₂ oxidation.

Using a Michaelis-Menten kinetic model, we found that increasing the H₂O coverage leads to a decrease in v_{max} , a term proportional to total number of active sites. This was spectroscopically supported by CO adsorption on Au using FTIR spectroscopy. We hypothesize that these are the sites closest to the metal-support interface, and that these sites are responsible for H₂ activation. This hypothesis was further supported by D₂ adsorption studies. Upon introducing D₂, we observed a decrease in OH stretching groups as well as a proportional increase in OD. DFT calculations confirmed that the most energetically favorable mode of H₂ activation on Au/TiO₂ is through heterolytic H-H cleavage, yielding a formal hydride on the Au and a proton on the support hydroxyl groups. The DFT calculated barrier for heterolytic cleavage (37 kJ/mol) agreed with the experimentally determined barrier for H₂ oxidation (28 ± 9 kJ/mol).

By using a full kinetic, spectroscopic and theoretical analysis, a new mechanism of H₂ activation on Au has been proposed. This has several practical applications. As an example, it further emphasizes the importance of maintaining one monolayer of H₂O for high PrOx performance (poisoning H₂ oxidation while promoting CO oxidation). Additionally, using these mechanistic insights, it may be possible to design more reactive Au selective hydrogenation catalysts, utilizing the knowledge that proton mobility and surface properties play an important role in hydrogen activation.

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24. Metal-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 metal-exchanged ZSM-5 is one of the promising technologies given the availability of ethylene feedstock. Here, we first present a systematic study on the influences of Ag species on ethylene DHA over Ag-ZSM-5.^[2] It was observed that Ag-ZSM-5 exhibits enhanced aromatic selectivity (~60%) compared to H-ZSM-5 (~20%) at similar ethylene conversion (at 400°C and 1 atm). These observations are qualitatively consistent with density functional theory (DFT) calculations that compare activation barriers and adsorption energies of ethylene and methane over H- and Ag-ZSM-5. We will also discuss the effect of Ga species on this reaction. Two different types of Ga-containing ZSM-5 (framework and extra-framework Ga) have been synthesized. Compared with Ag-ZSM-5, the extra-framework Ga-ZSM-5 shows a continuous increase in aromatic selectivity, while framework Ga-MFI exhibits a three-fold increase in catalytic lifetime; therefore, we proposed that different Lewis acids that reside either on the exterior surface or incorporate into the framework could promote distinct reaction activities. Collectively, these studies seek to improve the design of heterogeneous catalysts for non-oxidative upgrading of methane and light olefins.

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25. Transient Modes of Zeolite Surface Growth: Establishing New Platforms for Catalyst Design from Mechanistic Understandings of Crystallization

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Zeolites are widely used in commercial processes spanning from ion exchange in detergents to catalysis in the (petro)chemical industry. Understanding the mechanisms of zeolite growth at a molecular level aids the a priori selection of synthesis parameters to tailor their physicochemical properties. 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 challenging. Our group developed a way 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 Using this technique, we have identified methods to selectively control the pathways of growth² and manipulate the anisotropic kinetics of crystallization through the employment of crystal growth modifiers.³

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 the anisotropic rate(s) of growth to achieve desired crystal size and morphology. We have reported the efficacy of ZGMs in silicalite-1 bulk crystallization experiments.⁴ Here, we will discuss *in situ* AFM studies of ZGM effects on silicalite-1 crystals wherein 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. We show that these pathways can be influenced by the presence of ZGMs.

We will also present *in situ* AFM results of industrially relevant aluminosilicates (e.g., zeolite A) where we observe distinct growth regimes as a function of supersaturation and temperature. At high supersaturation and low temperature, we observe the three-dimensional assembly and structural evolution of gel-like islands on zeolite surfaces.⁵ These features, which derive from molecularly-dispersed solute, constitute a unique mode of growth among reported cases of nonclassical crystallization.⁶ Time-resolved imaging also reveals that growth can occur by (nearly) oriented attachment, which is a rare phenomenon for zeolites, but is observed during crystallization by particle attachment (CPA) for other minerals. We also report a distinct switch in the growth mode at moderate supersaturation and high temperature marked by two-dimensional nucleation of single layers with step heights corresponding to the composite building units of the crystal structure. Crystal growth in low supersaturation occurs by layers emanating from spiral dislocations. Interest in understanding zeolite A formation stems from its widespread use as a commercial molecular sieve; however, recent discoveries that zeolite A is an active catalyst for environmental applications and methanol to olefins reactions has placed this material in the spotlight.

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26. Exploring Novel Routes for Tuning Polymorphism and Elucidating Growth Mechanisms in Zeolites

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There has been increased interest to identify new commercially viable routes to produce zeolites with well defined properties. One such approach is seeded growth of zeolites. Indeed, it is well known that using a zeolite as a seed can expedite zeolite crystallization by reducing the induction time and reducing the formation of unwanted impurities. Seeding also provides a route to remove costly organic structure-directing agents (OSDAs) from the synthesis; however, the theory behind seeded growth is still unclear due to the inherent complexity of zeolite crystallization and the vast number of species in synthesis mixtures. Itabashi et al.¹ reported a working hypothesis on the basis of common secondary building units (SBU) between the seeds and zeolite product. At present, the direct characterization of such intermediates is not feasible. Our group developed a way to carry out solvothermal *in situ* atomic force microscopy (AFM) wherein we can observe zeolite surfaces at near molecular resolution under realistic growth conditions.² Even with AFM it is challenging to visualize growth by SBUs.

Previously, we used solvothermal AFM to study zeolite A (LTA) crystallization and found that it occurs via diverse modes of crystallization ranging from 3D gel-like islands to 2D layer-by-layer growth. We showed that the growth pathway is highly dependent on the selection of synthetic conditions.³ Here, we will present zeolite crystallization at low supersaturation where growth occurs by layers emanating from spiral dislocations, consistent with images of crystal surfaces removed from saturated growth solution.

We will also present the effect of seeds on interzeolite conversion/polymorphism. The effect of zeolite seed topology, seed content (weight percentage), synthesis time and temperature are studied to elucidate the mechanistic details of seeded growth and interzeolite transformation. We have utilized kinetic ternary phase diagrams to select the compositions for the seeds and growth solutions, thereby avoiding the formation of polymorphs.⁴ From these studies we have found that the seed phase is metastable, and can facilitate the formation of the same phase at short times; however, longer synthesis time often leads to the formation of more thermodynamically stable isostructures. To this end, seeded growth can be selectively tuned by controlling parameters such as synthesis time and temperature.

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27. Evaluation of the Benefits of Kinetic Monte Carlo and Microkinetic Modeling for Catalyst Design Studies in the Presence of Lateral Interactions

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Microkinetic models (MKM) are commonly used in catalyst, reactor and process design by solving ordinary differential equations within the mean-field approximation.¹ A more modern and powerful approach is provided by kinetic Monte Carlo (kMC) simulations of heterogeneously catalyzed reactions that integrate microscopic, mesoscopic and macroscopic levels into one multiscale simulation. A key advantage of kMC over traditional MKM is that it explicitly considers correlations, fluctuations, and spatial distributions of the adsorbed species on catalyst surface.

To evaluate the practical advantages of both methods for descriptor-based catalyst design studies we consider the prototypical CO oxidation reaction on close-packed fcc(111) surfaces,² and focus on the effect of lateral adsorbate-adsorbate interactions on the predicted activity trends.³ When the same elementary steps and rate constants are used in the absence of any lateral adsorbate-adsorbate interactions, both the kMC and MKM simulations result in identical CO oxidation mechanisms and activity trends. When lateral adsorbate-adsorbate interactions are explicitly accounted for, however, the simulation results for activity trends and surface coverages differ. By varying the rate constants for surface diffusion steps in the kMC model we are able to eliminate surface diffusion as possible origin of the differences; all diffusion steps are quasi-equilibrated and rapid surface rearrangement is kinetically feasible. Instead, the repulsion between CO* and O* enlarges the O* and O₂* covered region, but the interaction effect becomes less relevant at low coverages, i.e., for weakly binding species. Thus, the region of highest CO oxidation activity is found near less reactive metals.

In summary, we have assessed the strengths and weaknesses of MKM and kMC approaches for catalytic activity evaluation. We find that MKM is generally preferred because of its easier implementation and computational efficiency, but it is unreliable for cases with lateral adsorbate-adsorbate interactions or heterogeneous surfaces with multiple active sites. For these cases, a kMC simulation is the preferred choice.

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28. Mechanistic Study on C-C Coupling of Acetaldehyde on Partially Reduced CeO_{2-x}(111)

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Selective C-C coupling on earth-abundant solid materials such as ceria represents an effective way to upgrade small organic oxygenates into larger, more valuable chemicals. Surface science and model catalyst studies have reported that acetaldehyde can be readily converted into C₄ products, chiefly among which is crotonaldehyde, on ceria nanoparticles.^{1,2} However, temperature programmed desorption (TPD) of acetaldehyde on highly ordered stoichiometric or partially reduced CeO₂(111) and (100) thin film surfaces found little to no C₄ products under UHV conditions.^{3,4} To resolve this apparent discrepancy, we have examined several C-C coupling and crotonaldehyde formation pathways in detail theoretically, based on first-principles DFT calculations and microkinetic modeling. We will present evidence that crotonaldehyde can be formed on CeO₂(111) in UHV via a surface enolate intermediate^{5,6} and identify the active site on which the reaction occurs.

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29. Interaction of Thiol Ligands with Gold and Effects on Electrocatalytic CO₂ Reduction

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The electrocatalytic CO₂ reduction reaction (CO₂RR) has the potential to produce fuels and chemicals from a renewable feedstock. It can be used as an energy carrier to store energy generated from intermittent, distributed sources such as wind and the sun. It can also be used as a renewable source of carbon for chemical production. The key to enabling these uses of CO₂ is to maximize the selectivity and energy efficiency of electrocatalytic CO₂RR toward the desired product.^{1,2} We have taken inspiration from biological enzymes that catalyze CO₂RR (e.g. carbon monoxide dehydrogenase³) and attempt to mimic their active sites by functionalizing Au electrodes with a series of organic thiol ligands, to seek opportunities to potentially break the constraints imposed by scaling relations. Our work shows that different thiol species can enhance the activity for the formation of different CO₂ reduction products. For instance, 2-mercaptanpropionic acid effectively reduces the yield of CO to negligible amounts and enhances H₂ evolution to nearly 100% faradaic efficiency.⁴ On the other hand, 2-phenylethanethiol strongly promotes CO evolution and suppresses H₂ evolution.

We have performed detailed density functional theory calculations and theoretical modeling in conjunction with our electrochemical experiments to elucidate the role of the thiol ligands in CO₂RR on Au. We find that thiol ligands exist primarily as thiolates on Au in the potential range relevant to CO₂RR. They can readily reconstruct Au surfaces at ambient conditions, leading to a higher proportion of under-coordinated sites where the activity of CO₂ reduction is significantly promoted but the effect of under-coordinated Au sites on H₂ evolution is less prominent. Our study suggests that functionalization of Au holds significant promise for promoting CO₂ reduction and achieving different product selectivity with appropriately chosen ligands.

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30. Cooperative Lattice Oxygen Redox Catalyzing Nitric Oxide Oxidation

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An ideal catalyst for complete oxidation requires easy activation of O₂ molecule, active O adatom and thermally stable framework. Oxides with relatively strong bonded lattice oxygen is beneficial to O₂ activation and structure stability, but detrimental to individual O activity, which is known as scaling relations. However, we demonstrate that two nearby lattice oxygen with low activity on mullite SmMn₂O₅ united become active through a cooperative reaction pathway, therefore circumventing the fundamental limit. This new reaction mechanism opens a way to understand and design ideally active oxide catalyst for complete oxidation catalysis.



31. Methane activation using solid superacids

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Shale gas revolution has had a profound impact on the overall production of natural gas. This has resulted in new research in the area of conversion of methane, the principal component of natural gas. Activation of methane typically requires very high temperatures, e.g., indirect conversion of methane via syngas. Alternatively, direct conversion could greatly simplify the overall process. One direct conversion process involves the use of what is known as a “superacid”¹. A solid superacid catalyst has sufficient acidic strength to protonate methane and to subsequently break the C-H bonds, leading to higher carbon-number products. The overall reaction is:



Here, we present research focusing on the oligomerization of methane using a solid superacid catalyst based on HBr-AlBr₃. In an earlier work, this same catalyst was shown to convert ~99 % methane in the gas-phase². Another pathway could be aromatization of methane, forming benzene and hydrogen. Here, we present results from the aromatization of methane using Mo supported on sulfated zirconia, a well-known solid superacid.

Mo supported on sulfated zirconia was found to be active for methane dehydroaromatization around 600-700 °C. Presence of Mo₂C was confirmed using XPS and TEM and is generally thought to be the active site for methane activation³. Dimers produced by Mo₂C are cyclized/aromatized over Bronsted acid sites from sulfated zirconia.

Acknowledgement. The work on bromide based superacids was supported by Chevron via the Fund for Innovation in Engineering Research, supported directly to LSU and also through NSF Early Concept Grant for Exploratory Research (EAGER). The work based on sulfated zirconia is supported through LSU’s office of research and economic development.

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32. Tailoring the Aluminum Distribution in Zeolite ZSM-5 using Mixtures of Organic and Inorganic Structure-Directing Agents

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The spatial distribution of aluminum in zeolite crystals can influence their catalyst activity, selectivity and/or stability, irrespective of similar bulk elemental composition (Si/Al ratio).¹ Different post-synthesis methods have been developed to modify the aluminum distribution, but they often require multi-step treatment procedures and the use of expensive agents, which are not ideal for industrial applications.

A phenomenon known as aluminum zoning, where aluminum is preferentially located in the exterior rim of zeolite crystals, has been reported for ZSM-5 in many studies; however, its origin remains elusive.¹ To address this topic, we have performed parametric investigations to assess the role of synthesis conditions on the distribution of Al. We were able to develop a one-step synthesis method to prepare ZSM-5 crystals with either Si- or Al-rich exteriors. We also tested their catalytic performance for reactions, including biomass conversion and methanol-to-hydrocarbons. We were able to improve the selectivity and lifetime of the catalysts dramatically owing to their well-tailored core-shell structure.

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

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33. Acetylene, ethylene, and propylene oxidation on Pd/Ceria-Zirconia and Pd/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 ($\text{CeO}_2\text{-ZrO}_2$) 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 acetylene, ethylene, and propylene under near-stoichiometric conditions was studied using a Pd/Ceria-Zirconia and Pd/Alumina monolith catalysts. Acetylene, ethylene, and propylene were observed to be self-inhibiting. LO behavior improved with increasing catalyst ceria content. Mutual inhibition effects were also examined for mixtures of the three species. Steady-state kinetics measurements during individual species oxidation were conducted to find reaction orders and activation energies of oxidation.



34. Hydrogen peroxide production from hydroxylamine using palladium-decorated gold nanoparticle

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Hydrogen peroxide (H₂O₂) is widely used in daily life and industry. It is produced in large scale by the anthraquinone oxidation (AO) process. However, this process involves the use of organic solvent and energy-intensive liquid-liquid extraction to recover H₂O₂, which is not a green process and cost-effective. Thus, novel and greener methods for the production of H₂O₂ were explored. The direct synthesis of H₂O₂ from O₂ and H₂ gas using a variety of catalysts were reported, but these processes were possibly explosive and not safe for industrial operation. In this study, instead of using H₂ gas, we used a relatively safe liquid-phase hydrogen donor chemical - hydroxylamine to produce H₂O₂. In our process, the rapid and selective production of H₂O₂ can be achieved by the use of unique designed Pd-decorated Au catalysts.



35. Design of Diesel Oxidation Catalysts with Improved Activity at Reduced Temperature Using Computational Methods

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Low temperature combustion (LTC) diesel engines have higher fuel efficiency and produce less NO_x and particulate matters (PM) compared to traditional diesel engines. However, this benefit comes at the cost of higher concentrations of CO and unburned hydrocarbons (HC) emissions.¹ Meanwhile the low exhaust temperature results in a reduction in the activity of commonly used diesel oxidation catalysts (DOC). Thus, improved DOC with superior activity at reduced exhaust temperatures are needed.

In this work, a computational screening method is applied for quick catalyst discovery under different reaction conditions.² We propose that better low temperature DOC can be made by the alloys of coinage metals with Pt or Pd. Compared to the commonly used DOC which are Pt and Pd alloys, these coinage metal alloys will not only achieve higher activity at the reduced temperature, but also prevent the mutual inhibition between CO and NO oxidations. In addition, we build reactor models to optimize the DOC efficiency and catalysts loading. Since under real working conditions, the exhaust CO, NO and HC are oxidized along the DOC reactor and different reaction conditions require different catalyst compositions, the overall DOC performance can be improved by designing a DOC reactor with metal concentration gradients, where the local alloy formulation is optimized for the local temperature and exhaust gas compositions. With this optimized DOC, we are hoping to lead to significant advances to meet tailpipe emission regulations at the low exhaust temperatures of a LTC engine, which will enable the widespread use of LTC engines.

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36. PrMn₂O₅ Mullite-type Oxides as Low Temperature and Highly Efficient NO Oxidation Catalysts

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Catalytic oxidation of NO to NO₂ is a critical step in the abatement of NO_x and particulate matter from the exhaust of lean-burn engines, a reaction that currently uses platinum (Pt) as a catalyst. Due to the scarcity and high cost of Pt, it is valuable to develop catalysts using Earth-abundant elements. A novel catalyst based on SmMn₂O₅ mullite-type oxide is shown to have superior activity for NO oxidation over Pt and perovskite oxides.^{1,2} Here we present PrMn₂O₅ as a promising low temperature catalyst with higher NO conversion efficiency when compared to SmMn₂O₅. The PrMn₂O₅ and SmMn₂O₅ samples are synthesized by the hydrothermal method and the bulk and surface properties are characterized using X-ray diffraction, N₂ physisorption, and X-ray photoelectron spectroscopy (XPS), respectively. The nature and thermal stability of NO_x ad-species are investigated using *in-situ* Fourier-transform infrared spectroscopy and Temperature-programmed desorption (TPD) techniques. The O₂ TPD indicates facile desorption of lattice oxygen from PrMn₂O₅ at low temperatures. The NO catalytic activity shows higher conversion maxima for PrMn₂O₅ with 50% conversion temperature (T₅₀) achieved at 230 °C when compared to 275 °C for SmMn₂O₅. Moreover, PrMn₂O₅ also shows activity as low as 120 °C, which is significant during the cold start period of the engine. Density functional theory (DFT) calculations are employed to elucidate the superior activity of PrMn₂O₅ over SmMn₂O₅ by comparing their NO adsorption and desorption barriers and hence NO oxidation reaction pathways. The insight gained through the combination of experimental studies and DFT calculations should pave way to design better low-cost, low-temperature, and highly efficient NO oxidation catalysts based on mullite-type oxides.

(1) Wang, W., *et al.*; *Science* 337 (2012) 832-835.

(2) Thampy, S., *et al.*; *Catal. Today* (2017), <https://doi.org/10.1016/j.cattod.2017.05.008>.



37. Synthesis Method Effect on The Surface Chemistry and Oxidation Activity of RMn_2O_5 (R=Sm, Bi) Mullite-Type Oxidation Catalysts

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Transition metal oxides have been investigated as Pt catalyst replacements for many years with limited success. More recently, Mullite-type RMn_2O_5 oxides have been shown to have higher NO oxidation activity than Pt.¹ Here we aim to investigate the influence of the synthesis method on the surface and catalytic properties, by comparing SmMn_2O_5 and BiMn_2O_5 mullite-type oxides synthesized using two different routes: co-precipitation-calcination and hydrothermal methods. X-ray diffraction and Rietveld refinement analysis are used to confirm the crystalline phases. The N_2 physisorption technique is used to measure the surface area of the materials while Low Energy Ion Scattering (LEIS) is used for the first time to probe the surface atomic composition of the mullite materials. Using lower temperature, hydrothermal methods, SmMn_2O_5 and BiMn_2O_5 compounds show a 5-10 times increase in surface area when compared to the samples obtained using coprecipitation when followed by high temperature calcinations. However, the catalytic activity is found to increase only by up to 30%. We explain the observed difference in catalytic activities using LEIS results and density functional theory (DFT) calculations. DFT results show Sm to have a thermodynamically dominant Mn rich (010) surface, known for its high oxidation activity, while Bi is shown to favor Bi termination in the (010) direction.

An improved understanding of the relationship between synthesis and material properties should pave the way towards developing Mn-mullite as efficient NO oxidation catalysts for various real-world applications.

(1) Wang, W., G. McCool, et al. "Mixed-Phase Oxide Catalyst Based on Mn-Mullite (Sm, Gd) Mn_2O_5 for NO Oxidation in Diesel Exhaust." *Science* 337(6096): 832-835

38. Synthesis and Characterization of Bimetallic Cu/Zn-ZSM-5

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MFI-structured zeolites have been crucial tools for catalytic conversion of alkanes. Aluminum substitutions in the siliceous framework promote electron-deficient super-acid sites, which can then bind an array of guest molecules in the porous framework. The introduction of metal ion species by aqueous exchange into these acid sites has been shown to promote unique electronic structures which enable desirable activation chemistry. Two species of interest, Cu and Zn, provide important interaction with symmetric gas species such as CO_2 and H_2 . Adsorption-decoupling chemistry promises to lower the energetic barrier for broader CO_2 conversion, yielding semi-reduced products like acetic acid. This presentation describes the synthesis of bimetallic Cu/Zn-ZSM-5 and characterizes the product species. PXRD was used to confirm the original and exchanged MFI structures. UV-vis spectroscopy confirmed ion loading as well as oxide presence. DRIFTS was used to show selective NO binding on the coordinated metal sites within the pores.



A Brief History of the Southwest Catalysis Society

As recounted by **Joe W. Hightower**, Professor Emeritus, Rice University (April 2009)

B.S. '59 - Harding University; M.S. '61 and Ph.D. '63 - The Johns Hopkins University

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

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

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

In addition, catalysis groups were springing up at several universities, including surface science by the late John Mike White at the University of Texas, Jack Lunsford's and Wayne Goodman's highly productive groups at Texas A&M, Richard Gonzales at Tulane, Jim Richardson at U of H, Kerry Dooley at LSU, Tom Leland and me at Rice, and groups at other universities in the 5-state area. What was lacking? There was no formal mechanism



for these diverse groups to exchange information or get advice in the southwest. The time was ripe for an organization where catalysis could be openly discussed. Although much catalysis research is proprietary, enough was sufficiently open to create a stimulating environment for sharing mutual interests, many focusing on new ultra-high vacuum analytical equipment that was being rapidly developed.

The first thing we did was to organize an NSF-supported workshop at Rice which (not surprisingly) concluded that more funding was needed for research on catalysts for fuels, environmental protection (cat converters), chemicals, etc. At that time, demand was also great for new employees with catalysis training, but the supply was quite limited. This provided an occasion for the development of short courses to train industrial employees in heterogeneous catalysis. Several courses were started around the country. One of the most successful was started at Rice and has continued for more than 30 years through the University of Houston. It can be said, then, that **SWCS was instrumental in starting these heterogeneous catalysis short courses.**

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

In 1985, the Southwest Catalysis Society was again called on to host a five-day 9th North American Meeting (NAM-9) at Houston's Adam's Mark Hotel. This time, Jack Lunsford and Lynn Slauch were General and Vice Chair; I was Technical Program Chair. Most recently, the SWCS members organized the spectacular North American Meeting at Houston's downtown Hilton Americas Hotel in 2007, attended by over 1000 delegates from all over the world, "Celebrating Catalysis Texas Style." Kudos again to SWCS officers Kerry Dooley, Brendan Murray, Scott Mitchell, Michael Reynolds, Yun-Feng Chang, Michael Wong, and many, many others! **All told, the SWCS has hosted 3 national events now: 1971 (NAM-2), 1985 (NAM-9) and 2007 (NAM-20).**