



SOUTHWEST CATALYSIS SOCIETY

2019 SPRING SYMPOSIUM

Friday, April 26, 2019

O'Quinn Great Hall, Alumni Center
University of Houston

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The SWCS officers and I welcome you to the 2019 Southwest Catalysis Society Spring Symposium, Friday, April 26, 2019, at the O'Quinn Great Hall in the Alumni Center of University of Houston.

We are delighted to present seven invited speakers and 36 poster presentations at this year's symposium. The 2019 SWCS Excellence in Applied Catalysis Award will be presented. Furthermore, meritorious posters by students and postdocs will be identified with Best Poster Awards. See Page 3 for an outline of the Program.

The 2019 Spring Symposium registration fee is \$20 for students and post-doctoral researchers, and \$60 all other attendees. The fee includes North American Catalysis Society and SWCS annual membership dues, coffee/snack break, and lunch. We highly recommend online pre-registration at:

<http://swcatsoc.org/events>

For on-site registration we will only accept credit cards (Visa, MasterCard, Discover, and American Express) for the registration fee. Event tickets and receipts will be sent via e-mail, so please be prepared to enter your e-mail address when you register.

Please see Page 4 for meeting venue and parking locations.

If you have colleagues who cannot attend the Symposium and wish to continue their membership in the NACS/SWCS, please forward this program to them. Membership dues (same pricing as the registration fee above) and corporate donations should be sent to our Treasurer, Travis Conant (see contact information at left).

We hope you will join us, and enjoy the Symposium!

Ye Xu

Louisiana State University

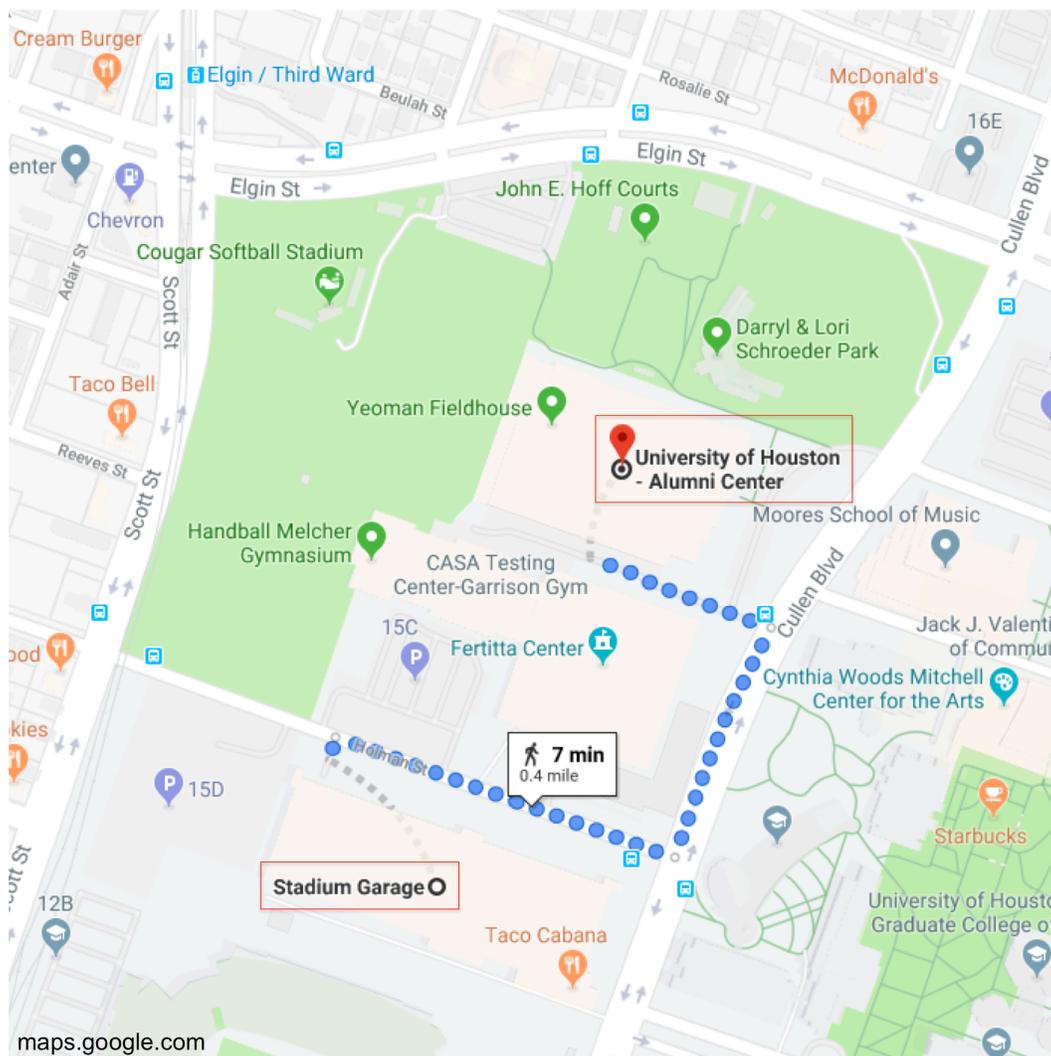
Chair



2019 PROGRAM

All talks, poster session, and coffee break/lunch will be held in the O'Quinn Great Hall.

- 7:30 AM** **Registration, check-in – Travis Conant, Treasurer**
- 8:10 AM** **Welcoming Remarks – Ye Xu, Chair**
- 8:15 AM** **Stu Soled**, ExxonMobil Research and Engineering Company, Corporate Strategic Research
Supported Bimetallic Noble Metal Catalysts Prepared with Bifunctional Organic Chelates
- 9:00 AM** **Phillip Christopher**, UC Santa Barbara, Department of Chemical Engineering
Controlling the Local Coordination and Reactivity of Oxide-Supported Atomically Dispersed Pt-Group Species
- 9:45 AM** **Coffee Break**
- 10:00 AM** **David West**, SABIC Technology and Innovation
Progress and Challenges in the Autothermal Oxidative Coupling of Methane
- 10:50 AM** **Sheima Khatib**, Texas Tech University, Department of Chemical Engineering
Enhancing the Catalytic Properties of Mo/ZSM-5 Catalysts for Methane Dehydroaromatization by Ex Situ Formation of Metal Carbides
- 11:35 AM** **Lunch Break (Catered) and Poster Session**
- 1:35 PM** **John Lockemeyer**, Shell Catalysts & Technologies
Winner, 2018 SWCS Excellence in Applied Catalysis Award
The Shell Ethylene Oxide Catalyst Journey
- 2:20 PM** **2019 SWCS Excellence in Applied Catalysis Award, Luo Lin**, Director, Award Selection Committee
- 2:35 PM** **Ya-Huei (Cathy) Chin**, University of Toronto, Department of Chemical Engineering and Applied Chemistry
Catalytic Significance of Proton-Hydride Pair during Hydrogenation of Strong Bonds
- 3:20 PM** **Thomas Senftle**, Rice University, Department of Chemical and Biomolecular Engineering
Identifying Physical Descriptors for Predicting Metal-Support Interactions in Catalysis with Density Functional Theory and Statistical Learning
- 4:05 PM** **Poster Awards, Praveen Bollini**, Director
- 4:20 PM** **End**



Symposium location:

O'Quinn Great Hall
UH Alumni Center
3204 Cullen Blvd, Houston, TX 77004

Recommended parking location (\$14 per day):

UH Stadium Garage
3874 Holman St, Houston, TX 77004

Supported Bimetallic Noble Metal Catalysts Prepared with Bifunctional Organic Chelates

Stu Soled

ExxonMobil Research & Engineering Co, Corporate Strategic Research

Supported metal oxides, metals and sulfides form a large fraction of industrially important catalysts. We will detail different preparation approaches all aimed at controlling active site number and site location, particularly on bimetallic noble metal supported catalysts. Issues involving activity, transport, metal mixing and deactivation come into play. Site locations must be optimized on both mm and nm scale. The primary approach we will illustrate involves surface complex formation using bifunctional organic chelating agents, an approach that provides a scalable synthesis route, particularly for noble metal and alloy catalysts on silica.

We will describe our initial motivation to explore this approach for preparation of well-dispersed Ru catalysts on silica and how that study expanded into exploring other noble metals (Ir, Rh and Pd) on silica and more recently into studies of bimetallic systems. In the most current work, we focus on two bimetallic systems, supported Pt-Pd and Ru-Rh, and we will describe what we have learned about their morphological and catalytic properties.



Biography

Stu Soled attended City College New York where he received his B.S. degree in chemistry in 1969. Following that he pursued his Ph.D. in chemistry from Brown University in 1973. He then did 4 year of post-doctoral work in solid state chemistry both at Brown University and in France, focusing on the synthesis and characterization of novel oxide and sulfide materials. He has been at Exxon's Corporate Research Labs for over 38 years and currently holds the position of Distinguished Research Associate. His research interests lie in the synthesis, characterization and evaluation of novel catalytic materials. He has worked extensively on Fischer-Tropsch chemistry, solid acid and metal catalysis, and hydrotreating. He is the coauthor of more than 70 publications and over 100 U.S. patents. Stu is the recipient of the New York Catalysis Society Excellence in Catalysis Award, the North American Catalysis Society Frank Ciapetta Lectureship Award, the ACS Heroes in Chemistry Award, the Herman Pines Award in Catalysis, the Distinguished Researcher Award in Petroleum Chemistry from the Division of Energy and Fuels of the American Chemical Society and in 2014 he became a member of the National Academy of Engineering in recognition of his contribution in discovery of new commercialized hydroprocessing catalysts that have created a new paradigm in an old area.

Controlling the Local Coordination and Reactivity of Oxide-Supported Atomically Dispersed Pt-Group Species

Phillip Christopher

Department of Chemical Engineering, University of California, Santa Barbara

The synthesis of oxide supported Pt-group catalysts typically produces metal particles with dimensions of a few nanometers. Recent work has shown that Pt-group species can co-exist as nanoparticles and single atoms, and that careful synthetic approaches can produce exclusively single atoms. Interest in the reactivity of supported isolated Pt-group metal atoms stems from the maximized metal utilization efficiency, unique reactivity or selectivity, connection to organometallic catalysis, and the potential for making well-defined active sites. It has proven challenging to characterize the intrinsic catalytic activity of these dispersed active sites on oxide supports at a level that relates local electronic and geometric structure to function. The difficulty arises from their atomic dispersion, heterogeneity in the local coordination of active sites on most catalysts (i.e. isolated species sit at different sites on the support), dynamic changes in local coordination under reactive environments, and often the low loading of metal that is required to achieve site isolation.



In this talk I will describe a synthetic approach to produce isolated Pt-group atoms that exhibit uniformity in their bonding environment on an oxide support and show how a combination of microscopy, spectroscopy and theory can be used to describe the local coordination of these species. Then I will describe two different approaches to control the local environment of Pt-group atoms: (1) through varied pre-treatment that tunes the local coordination and oxidation state of the single atom, and (2) through the addition of inorganic and organic functional groups on the oxide support surrounding the Pt-group atoms. Detailed characterization by a combination of spectroscopy and microscopy is used to develop structure-function relationships for these well-defined single atom active sites in the context of CO oxidation, alkene hydroformylation and methanol carbonylation. This work highlights the ability to tune the local environment of single Pt-group atom active sites on oxide supports in analogous ways to the engineering of organometallic catalysts

Biography

Phillip Christopher received his B.S. from University of California, Santa Barbara in 2006 and his M.S and Ph.D. from University of Michigan in 2011, all in Chemical Engineering. From 2011-2017 he was an Assistant Professor at University of California, Riverside. In 2017 he moved with his group to the University of California, Santa Barbara where he is an Associate Professor in the Chemical Engineering Department and the Mellichamp Chair in Sustainable Manufacturing. He also currently serves as an Associate Editor for ACS Energy Letters. His research interests are in heterogeneous catalysis, *in-situ* characterization of the dynamic behavior of catalysts, and photocatalysis by metal nanostructures. Phillip has won various awards including the Young Scientists Award from the International Congress on Catalysis, Army Research Office Young Investigator Award, NSF Early CAREER Award and the Early Career Award for Scientists and Engineers from the Army (ECASE-Army).

Progress and Challenges in the Autothermal Oxidative Coupling of Methane

David West

SABIC Technology and Innovation

For 40 years, scientists have sought to develop a high yield process for oxidative coupling of methane (OCM). Recently we have shown that autothermal operation (AO) is feasible with feed temperature as low as 298 K [Sarsani et al. *Chem. Eng. J.* 328 (2017) 484]. One of the difficulties encountered in scaling up laboratory experiments to larger reactors is the reduction in size of the feasible region for AO caused by heat loss. Another is the non-monotonic change in conversion and selectivity as function of feed flow rate or space-time. In this talk, I will describe some principles and challenges for design of an autothermal OCM reactor.



Biography

David West is a Corporate Fellow at SABIC focused on the development of new process technologies and differentiated products. He joined SABIC in 2012 after 31 years with The Dow Chemical Company. His interests include development of new materials, reaction engineering, fluid dynamics, transport phenomena, and non-linear dynamics. David is an editor of the book series, *Advances in Chemical Engineering*, member of the Industrial Advisory Board for University College of London, Consulting Editors Board for *AICHE Journal*, past member of the Board of ISCRE, co-chair for the NASCRE3 and MACKIE2 conferences, and adjunct professor in the Department of Chemical and Biomolecular Engineering at the University of Houston. He received the 2012 AIChE Catalysis and Reaction Engineering Division Practice Award, and a Chemical Engineering Science most cited paper award.

Enhancing the Catalytic Properties of Mo/ZSM-5 Catalysts for Methane Dehydroaromatization by Ex Situ Formation of Metal Carbides

Sheima J. Khatib

Texas Tech University, Department of Chemical Engineering

Finding new uses for methane as a fuel and chemical feedstock in the manufacturing industry is of increasing interest since methane is the main constituent of natural gas, of which vast natural reserves are being exploited. Large quantities of this natural resource are being flared due to lack of infrastructure and high transportation costs. Among the different direct processing reactions that exist to convert methane to value-added products, there has been a growing interest in the heterogeneous catalytic conversion of methane to a mixture of benzene and hydrogen, by the non-oxidative methane aromatization reaction ($6 \text{CH}_4(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{g}) + 9\text{H}_2(\text{g})$), which happens in one step. Our group is carrying out a fundamental and systematic study of this catalytic process with the goal to answer some fundamental questions, which can mitigate the technological challenges of this process.



Zeolite-supported molybdenum catalysts have so far been the most widely studied catalysts for the methane aromatization reaction, however, they do not fulfill the conversion and stability requirements for commercialization. It is agreed that Mo carbide species, originated by exposure of the Mo oxide species to the reactant methane, are responsible for methane activation, however, the nature and amount of carbide phases formed in the induction period of the reaction are not controlled. Our group has recently discovered the importance of the conditions at which the zeolite-supported molybdenum carbides are formed on the catalyst stability. We have tested different preparation conditions and contrasted the structure of the fresh and spent catalysts to explain the difference in catalytic behavior. Our results have resulted in obtaining Mo/ZSM-5 catalysts that maintain remarkably stable benzene yields over long periods of time in reaction.

Biography

Sheima J. Khatib joined the Department of Chemical Engineering at Texas Tech University as tenure-track Assistant Professor in Spring 2015. She received her PhD in Chemistry under the guidance of Miguel Angel Bañares from the Autonomous University of Madrid and the Institute of Catalysis and Petrochemistry (CSIC) in 2007. She continued her research from 2008-2010 in the Institute of Physical Chemistry “Rocasolano” also in Madrid, with Jose Maria Guil, and then moved to Virginia Tech to work in the group of Ted Oyama. Her expertise is in studying structure-activity relationships, adsorption microcalorimetry and membrane technology applied to heterogeneous catalysis. Her main areas of interest are natural gas conversion, dehydroaromatization, bio-inspired catalysts for heterogeneous chemical conversion, catalyst stability, strategies for regeneration and deactivation pathways. Sheima is also passionate about exploring new engineering education methods in her classes and places much emphasis on teaching, having received five teaching awards including the 2017 George T. and Gladys Abell-Hanger Faculty Award at Texas Tech University and the 2017 and 2018 AIChE student chapter awards, also at Texas Tech. She has given 9 invited lectures, published 21 peer-reviewed articles, and serves on the board of directors of the Southwest Catalysis Society, the Fuels and Petrochemicals Division (AIChE) and the Catalysis and Reaction Engineering Division (AIChE).

The Shell Ethylene Oxide Catalyst Journey

John Lockemeyer

Shell Catalysts & Technologies

This presentation will offer an overview of some of the significant contributions by Shell scientists, engineers, and technical staff to the field of ethylene oxide (EO) production. Starting with Shell's involvement in silver based EO catalysts dating back to the 1930's and culminating in the deployment of our most recent achievement in the High Performance EO Process, the journey through the approximately 87 inventive years will be described.

In the second half of the lecture a deeper dive into an example of some fundamental science will be presented. Here the problem of silver particle sintering will be addressed with an illustration of the many tools employed to tackle a very difficult question: What is the mechanism of sintering in EO catalysts? This deceptively simple question inspired experimental work involving many approaches - including bulk catalysts, spin-coated model catalysts, electron beam lithography, and DFT/Monte-Carlo atomistic computations. This illustrates the level of sophistication employed at Shell Catalysts & Technologies in the development of modern-day ethylene oxide catalysts



Biography

John Lockemeyer is a research scientist at Shell Catalysts & Technologies. He earned his B.S. in Chemistry at Villanova University in Philadelphia, PA in 1982. John then went on to earn his Ph.D. in Inorganic Chemistry at the University of Delaware in 1987, his thesis focused on the synthesis and reactivity of heterobinuclear metal complexes as homogeneous hydroformylation catalysts. During a post-doctoral research appointment at the University of Illinois Urbana-Champaign, John investigated synthetic routes to organometallic metal sulfides as models for heterogeneous metal sulfide based refining catalysts. John then moved to Houston and joined the Catalysis Department at Shell in 1989. During his career at Shell he has been involved in multiple technology areas, including hydrocracking, hydrotreating, epoxidation, acetoxylation, OCM, and Gas-to-Liquids. He has served as session chair for the 2007 North American Catalysis Society Meeting, the elected Chair of the 2010 Gordon Conference on Inorganic Chemistry, and in 2016 was appointed as Principal Technical Expert for Selective Oxidation within Shell. Most recently John was honored with the appointment at Shell as a Senior Principal Science Expert. He currently is listed inventor on 36 issued US patents, 35 European patents, and has several journal publications. In his work, John enjoys collaborating globally with fellow scientists at industrial, academic, and government laboratories on projects ranging from fundamental R&D to commercial deployment of invention. John and his wife Molly have two beautiful daughters, Jennifer (26) and Lauren (24). In his off-time John enjoys fishing, skiing, and hiking.

Catalytic Significance of Proton-Hydride Pair during Hydrogenation of Strong Bonds

Ya-Huei (Cathy) Chin

University of Toronto, Department of Chemical Engineering and Applied Chemistry

Hydrotreating, hydrodeoxygenation, and hydrogenation reactions are important reactions in industrial fuel and chemical processes. These reactions involve the activation and sequential transfer of reactive hydrogen species to reactants and occur effectively on transition metal, sulphide, and oxide catalysts. Despite significant research effort, the details on the electronic charges, chemical identity, and resulting hydrogen addition paths have not been rigorously established. Here, I describe a generalized mechanism for the hydrogen addition events and their catalyst requirements for these different classes of reaction systems. Hydrogenation of heteroarenes (e.g., pyridine, pyrrole) and hydrodeoxygenation of phenolics both require an initial hydrogenation, which breaks the strong aromatic ring of arenes, followed by hydrogenolysis reactions. On metal sites with vicinal base ligands, hydrogen activates heterolytically, forming a proton-hydride pair. This reactive proton-hydride pair undergoes sequential hydrogen addition steps that transfer first a proton and then a hydride onto the aromatic rings, breaking their strong aromaticity. Similarly, on transition metal clusters, the solvent layers promote the formation of protons, which exist in equilibrium with the hydrogen adatoms. Both types of hydrogen species are required to complete the hydrodeoxygenation reactions of phenolic species that lead to the eventual C-O bond cleavage. This mechanistic framework captures both the effects of basic ligands (sulfur, oxygen) on catalyst surfaces as well as of solvent layers on catalytic rates and selectivities.



Biography

Ya-Huei (Cathy) Chin is an Associate Professor of Chemical Engineering and Applied Chemistry at the University of Toronto. She is a Canada Research Chair (Tier II) in Advanced Catalysis for Sustainable Chemistry (2016). She is recognized as an Emerging Leader in Chemical Engineering (2017), an award given by the Canadian Society for Chemical Engineering (CSChE), and a recipient of Humboldt Research Fellowship (2018), Ontario Early Researcher Award (2014), and Imperial Oil University Research Award (2014). She also received the Bill Burgess Teacher of the Year Award for Large Classes (2016). She joined the University of Toronto in 2011, after receiving her Doctor of Philosophy (Ph.D.) degree in Chemical Engineering from the University of California, Berkeley. She was a research engineer (2000-2002) and then senior research scientist (2002-2005) at Pacific Northwest National Laboratory (PNNL), one of the ten National Research Laboratories for the U.S. Department of Energy. Her recent work focuses on elucidating the molecular events during alkane oxidation on Group VIII metal clusters and conversion of oxygenates to value-added chemicals and liquid fuels. Specifically, she applies isotopic, kinetic, and density functional theory methods to study the dynamics of catalyst surfaces and catalytic pathways.

Identifying Physical Descriptors for Predicting Metal-Support Interactions in Catalysis with Density Functional Theory and Statistical Learning

Thomas P. Senftle

Rice University, Department of Chemical and Biomolecular Engineering

The performance of heterogeneous catalysts featuring metal nanoclusters on oxide supports can be significantly impacted by interactions between the metal and the support. In particular, charge transfer at the metal-support interface can alter the oxidation state of the metal, which in turn affects the reactivity of sites on the metal cluster. Identifying physical descriptors for predicting the extent of these electronic metal-support interactions (EMSIs) is imperative for tuning the overall activity, selectivity, and stability of many common catalytic materials. Such descriptors, which can be derived from readily-available physical properties of the metal and the support, enable one to predictively screen for metal-oxide pairs with interaction characteristics that are well-suited to the catalyst's reaction environment. In this work, we employ density functional theory (DFT) together with screening approaches derived from statistical learning (SL) to identify general descriptors for predicting the nature of EMSIs in metal-oxide catalysts. DFT is used to generate adsorption energy and charge distribution data for a wide range of metals and supports in the presence of various support-modifying dopants and adsorbates. This data then serves as the training set for SL screening tools that scan the feature-space of candidate descriptors for properties (e.g., electronegativity, ionization potential, electron affinity, etc.) that correlate with both charge transfer and adhesion strength between metals and supports. This methodology provides models for modifying supports to control EMSIs and enhance catalyst performance.



Biography

Thomas Senftle joined the Department of Chemical and Biomolecular Engineering at Rice University as an Assistant Professor in 2017. He earned his doctorate in chemical engineering at the Pennsylvania State University in 2015, where he worked with advisors Mike Janik and Adri van Duin on metal-oxide catalysts for hydrocarbon activation. He completed postdoctoral research at Princeton University working with advisor Emily Carter on the computational design of semiconductors for photo-electrochemical applications. Thomas's current research focuses on the development and application of computational modeling tools for assessing multi-component catalysts at both the electronic and the atomistic scale. Emphasis is placed on identifying fundamental structure-activity relationships that can inform the rational design of catalytic systems for efficient energy conversion, storage, and utilization. In 2018, he received a Doctoral New Investigator Award from the American Chemical Society's Petroleum Research Fund for work on iron-based catalysts for propane dehydrogenation.

POSTER ABSTRACTS

1. Tailor-Made Ag-based Catalysts for the Non-Oxidative Dehydrogenation of Methanol to Formaldehyde

Quan K. Do, Cindy Mai, and Lars C. Grabow*

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Formaldehyde is a critical and commercially relevant chemical building block for chemical derivatives such as resins, plastics, and butanediol. Based on data estimates from the United States Bureau of Labor Statistics, the American Chemical Council estimated that formaldehyde and its chemical derivatives accounted for 483 billion dollars in sales in 2014, or almost 3% of the United States gross domestic product in that year.¹ Historically, formaldehyde has been produced industrially via the catalytic conversion of methanol. Originally, silver gauze or crystals were used as dehydrogenation catalysts for the endothermic reaction $\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}_2$, which would be performed at temperatures from 600-720°C and a pressure of 1 MPa.² Today, the industry is now dominated by the newer Formox process, which is run under an excess of air and promotes the selective oxidation of methanol to formaldehyde. The catalytic non-oxidative dehydrogenation process remains highly desirable, however, due to high capital and energy costs affiliated with the massive use of air and the separation of trace formaldehyde from the product steam, as well as the wanted production of hydrogen as a byproduct.

It has been well-established, experimentally and theoretically, that different metal facets exhibit different catalytic behaviors. By understanding the different behaviors of the adsorbates on the different facets, different rates of reaction can be drawn from the different surfaces and aggregated into a model that would allow for the optimization of the nanoparticle size. In this work, using density functional theory (DFT), the non-oxidative dehydrogenation of methanol and its side reactions are studied on the (100), (111), and (211) surfaces of silver. The data obtained from these studies are input into a kinetic Monte Carlo (kMC) model that combines all three facets, and the terrace lengths of the (100) and (111) facets are altered to optimize the rate of formaldehyde production. Using Wulff constructions, the optimal size and shape of the Ag nanoparticles are predicted.

Furthermore, various metal promoters can be doped onto the surface to modify the behavior of the Ag catalyst. Single-atom alloy catalysts are a relatively new class of catalysts that can give unprecedented performance due to both the facile dissociation of reactants and the weak binding of intermediates.³ Our Ag(111) facet is decorated by palladium and zinc promoter atoms, which were determined to be structurally stable in the single-atom alloy configuration. We find that the palladium and zinc promoters improve the activity of the Ag(111) surface by binding hydrogen adatoms and methoxy groups respectively, indicating that the utility of single-atom alloys is a viable strategy for the improvement of the methanol dehydrogenation process.

- (1) The American Chemical Council. Formaldehyde Producers Boost U.S. Economy (2014).
- (2) Kent, J.A. Handbook of Industrial Chemistry and Biotechnology: v. 1 and 2 (2012).
- (3) Giannakakis, G.; Flytzani-Stephanopoulos, M.; Sykes, C.E.; Acc. Chem. Res. 52 (2019) 237-247.



2. Tuning ZSM-11 catalyst performance in the methanol-to-hydrocarbon reaction

Thuy T. Le, Heng Dai, and Jeffrey D. Rimer*

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Methanol-to-hydrocarbon (MTH) is an important process in petrochemical production from alternative sources. A key factor in improving MTH catalyst performance lies in the synthesis and design of heterogeneous zeolite catalysts. Notably, ZSM-11 is a promising catalyst not currently commercialized but has been shown to have better performance than its commercial counterpart ZSM-5.¹ In this study, we focus on ZSM-11 and seek to understand the effect of passivating external surface acid sites on catalyst stability and selectivity. Reactions at external surface sites are non-shape-selective² and can lead to external coking, i.e., pore blockage due to the formation of polyaromatic molecules.³ In addition, Weckhuysen⁴ has illustrated that deactivation by coking starts at the external region for ZSM-5, further justifying the importance of limiting surface reactions. An approach to passivating external acid sites has been reported as early as 1978 in a Mobil patent, followed by various methods of generating amorphous or crystalline overlayers on zeolites to suppress the external surface catalytic activities. However, well-structured (i.e. epitaxial) layers are required to prevent the narrowing of pore openings, which can lead to improved selectivities but at the cost of reduced activity owing to increased diffusion limitations.² The effects of these competing factors on catalytic performance have not been fully explored due in large part to a lack of control over passivating layer thickness. Here, we introduce an alternative method, adapted from a prior study of ZSM-5s, to generate core-shell structures in which siliceous ZSM-11 (silicalite-2) is epitaxially grown over an aluminosilicate zeolite core to create ZSM-11@silicalite-2 with continuous core-shell pore alignment and tunable shell thickness. In this study, a set of core-shell samples with a range of shell thicknesses were generated and tested in MTH reactions to analyze the various competing factors (i.e., external coking suppression, improved selectivity, tailored mass transport limitations) that putatively affect catalyst performance. Our results indicate a correlation between shell thickness and catalytic performance, wherein we identify an optimal shell thickness (ca. 10 nm) that leads to enhanced catalytic stability. Our findings also demonstrate the importance of controlling the Si content and shell thickness in the design of zeolite catalysts for MTH reactions.

(1) Rimer, J. D. et al.; *ACS Catal.* 8 (2018) 11042-11053

(2) Reitmeier, S. J.; Gobin, O. C.; Jentys, A.; Lercher, J. A.; *J. Phys. Chem. C* 113 (2009) 15355-15363

(3) Olsbye, U. et al.; *J. Catal.* 249 (2007) 195-207

(4) Weckhuysen, B. M. et al.; *Chem. Eur. J.* 14 (2008) 11320-11327

(5) Ghorbanpour, A.; Gumidyala, A.; Grabow, L. C.; Crossley, S.P.; Rimer, J. D.; *ACS Nano* 9 (2015) 4006-4016



3. Ternary Rare-Earth – Transition Metal Catalysts for Dry Reforming of Methane and Characterization of Final Structures and Sulfur Tolerance Evaluation

Changyi Jiang, Jaren Lee, and Kerry M. Dooley*

Cain Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803

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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 (1:1 CH₄:CO₂, 725-775°C) are used to identify doped TM-REO (e.g., Ni/Ce-Zr) systems that can be tolerant of sulfur and water at realistic levels. Our study shows that both Ni and Ni-Co containing catalysts outperform other dopant metals (Ru, Mn, Fe, etc.) in activity and coking resistance. Both can also maintain their activity over several days testing. However, in the presence of sulfur (0.07 or 20 sulfur in the feed) indicates that Co is necessary to improve the sulfur tolerance. XANES on spent catalysts also shows that while the bulk oxidation state of Ni in Ni/Co/Ce/Zr catalysts is reduced during the dry reforming reaction, to near zero-valent state, this bulk reduction is not accompanied by a change in activity. This in turn suggests that the Ni active sites are a distinct minority, associated with strong interaction with the Ce/Zr oxide. Other characterization evidence supports this hypothesis.



4. Bifurcation Analysis of Coupled Homogeneous-Heterogeneous Reactions in Monolith Reactors

Bhaskar Sarkar and Vemuri Balakotaiah*

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The steady state behavior of thermally coupled homogeneous-heterogeneous reactions in monolith and gauze reactors are studied using bifurcation analysis. The main objective of this study is to determine the impact of operating and design parameters such as inlet feed temperature, inlet feed ratio, space time, pressure and channel hydraulic radius on the ignition-extinction behavior of the reaction system. We use Oxidative Coupling of Methane (OCM) as a test example and use a global kinetic model consisting of seven reactions in heterogeneous (catalytic) phase and five reactions in homogeneous (gas) phase to investigate the bifurcation behavior.

Our results show that it is possible to obtain ~80% C₂ selectivity with ~20% CH₄ conversion for inlet CH₄/O₂ mole ratio of 6-8 and space time of 0.01-0.1s using La₂O₃/CaO catalyst. Higher CH₄/O₂ mole ratios lead to higher selectivities at the cost of lower CH₄ conversion and lower productivity. Operations on external mass transfer controlled regime (higher channel radius) result in higher selectivities but again lead to lower conversion. On the ignited branches the exit fluid temperature is found to be low enough (~1000K) to conduct stable autothermal operation of OCM.



5. Effects of Diffusional Constraints on Lifetime and Selectivity in Methanol-to-Olefins Catalysis on HSAPO-34

Heng Dai¹, Thuy Thanh Le¹, Andrew Hwang², Zhichen Shi², Aditya Bhan², Jeffrey D. Rimer^{1*}

¹ Department of Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204

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*jrimer@central.uh.edu

Methanol-to-olefins (MTO) catalysis on zeolites or zeotypes occurs via a complex reaction network referred to as the hydrocarbon pool (HCP).¹ The use of small-pore zeotypes, such as HSAPO-34 (CHA type), adds further complexity owing to the diversity of active sites for catalysis within the zeolite framework. Understanding the reaction-transport phenomena in complex reaction networks and improving catalytic performance via optimized diffusion properties are critical objectives in MTO catalysis.

Reaction-transport formalisms show that the effects of crystallite size, H⁺ density, and Si speciation of HSAPO-34 on catalyst lifetime and selectivity in MTO catalysis are all manifestations of diffusional constraints regulated either by structural catalyst properties or intrinsic kinetics. Defined quantities of total turnovers and cumulative selectivity provide rigorous assessments of lifetime and selectivity that permit causative correlation between rates of reactions within the complex network of autocatalytic reactions and material properties of HSAPO-34. Total turnovers decreases with increasing diffusional constraints as the dehydrocyclization reactions experience stronger diffusional constraints than reactions producing light olefins.

Hierarchical SAPO-34 zeolites exhibiting excellent catalytic performance have received increasing attention.² Here, we will present our preliminary research on generating hierarchical SAPO-34 catalysts with uniform intracrystalline mesopores through the use of crystal growth modifiers (porogens) such as polyethyleneimine, a dendrimer comprised of numerous amine functional groups. These materials are being explored for their potential to reduce mass transport limitations for MTO reactions.

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6. Low Temperature CO₂ Conversion by Earth Abundant Perovskite Oxides via Thermochemical Looping Process

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The current global energy and environmental scenario has led to significant efforts on sustainable energy generation and utilization. Atmospheric carbon dioxide reduction and repurposing towards hydrocarbon generation has garnered a lot of attention over the last decades. While solar thermochemical (STC) CO₂ conversion has shown a lot of promise [1], it is limited for large scale industrial application by its high temperature of operation (more than 1000 °C) and the catalyst stability at these temperatures. Reverse water gas shift chemical looping (RWGS-CL) process, a modified version of STC, hereby presents the benefits of STC along with low temperature operation [2]. Perovskite oxides (ABO₃) have also demonstrated great performance in RWGS-CL process. The key step of RWGS-CL is the formation of oxygen deficient materials that are highly active towards CO₂ conversion to CO [3]. Using density functional theory (DFT) calculated oxygen vacancy formation energies as appropriate descriptors of this process, we screened a large composition space of perovskite oxides. The predicted materials were experimentally synthesized via Pechini method and tested in RWGS-CL process. We observed exceptional CO₂ conversion performance of several perovskite oxides [4]. Lowest temperature of operation was found to be 450 °C, thus enabling thermal integration with subsequent CO-hydrogenation processes such as Fischer Tropsch. These new perovskite oxides were found to be stable for several cycles of operation, allowing for large scale industrial application. Moreover, being earth abundant, these materials provides opportunities for low-cost catalyst synthesis. An empirical model was also developed for oxygen vacancy formation energy as a function of intrinsic material properties for future materials discovery.

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7. Nature of Active Sites for Passive NO_x Adsorption on Pd-SSZ-13

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Pd- exchanged zeolites exhibit a variety of dynamically changing active sites that contribute to their performance as passive NO_x absorbers (PNA).¹ In particular Pd-H-SSZ-13 with the 8-member ring chabazite,(CHA) framework is a promising material for trapping NO at cold start temperatures and releasing NO and NO₂ (NO_x) at elevated temperature. We combine molecular computations (density functional theory, DFT) with experiments (NO uptake and temperature programmed desorption, TPD; Temporal Analysis of Products, TAP) to identify the types of active sites on 1% Pd-SSZ-13, to understand their transient response to temperature and feed changes, and to formulate viable mechanistic pathways steps that lead to NO_x trapping and release.

DFT computations indicate that the strongest binding sites for NO are partially reduced ZPd^I sites. In the absence of water NO binding strongly on ZPd^I with a heat of adsorption of -250 kJ/mol in the absence of H₂O and only slightly lower (ca. -200 kJ/mol) in the presence of water. The ZPd^I site, however, is not as stable as the ZPd^{II}OH or Z₂Pd^{II} sites, featuring Pd mostly in latter forms. With NO as the only reductant present in the feed, the formation of reduced ZPd^I active sites from ZPd^{II}OH requires ca. 140 kJ/mol. This reduction process proceeds first by an endothermic dehydration of two ZPd^{II}OH sites to form a ZPd^{II}-O-Pd^{II}Z bridging species, followed by the reduction with NO to two ZPd^I sites. In contrast, the presence of a stronger reductant such as CO, H₂ or ethylene renders the reduction energetics more favorable. In the case of CO, the ZPd^I site is actually ~35 kJ/mol more stable than the ZPd^{II}OH site and an increase in NO uptake is expected.

Sequential NO uptake at 100°C and NO_x TPD under a 20°C/min temperature ramp in the presence of H₂O reveal excellent NO trapping with the NO: Pd ratio of ~1. Water deters NO_x uptake on Bronsted acid sites but the Pd sites remain effective. The addition of CO or ethylene (C₂H₄) as co-reductant significantly increases the NO uptake. Isotopic labelling studies in the TAP reactor² in the temperature range of 100°C - 450°C confirm the production of ¹⁵N¹⁶O¹⁸O and ¹⁵N¹⁶O after the catalyst was pretreated with ¹⁶O₂ and pulsed with ¹⁵N¹⁸O. The incorporation of the labelled oxygen is consistent with the postulated reduction step from DFT.

Our detailed mechanistic insight into the elementary steps describing the dynamic changes of active sites during NO trapping and NO₂ production suggests that the relative stability of reduced, oxidized and hydrated/hydroxylated cationic sites is paramount. This knowledge provides the basis for future improvements of PNA materials.

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8. Dehydroaromatization of Ethylene over Silver-exchanged ZSM-5: Insights from Transient Kinetics Experiments and Density Functional Theory Simulations

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Aromatic hydrocarbons such as benzene, toluene and xylene (BTX) are important commodity chemicals that are used as fuel additives and as raw materials in the synthesis of specialty chemicals, amongst other uses [1]. The surge in natural gas production across the world has incentivized the search for processes that can utilize methane and light olefin derivatives in the manufacture of aromatic products. While the functionalization of methane occupies the minds of industry and academia alike, a process that has only recently garnered attention is the zeolite-catalyzed conversion of ethylene to aromatics. The use of Lewis acids expands the applicability of zeolite catalysts into such processes [2]. Here, we examined Ag-ZSM-5 as a catalyst in the dehydroaromatization (DHA) of ethylene through temporal analysis of products (TAP) transient kinetics experiments and density functional theory (DFT) calculations.

The state of Ag in the ion-exchanged Ag-ZSM-5 catalyst was identified as a Lewis acid cation, either bound to an isolated Al or second nearest neighbor Al-pairs. *Ab initio* UV-vis simulations and measurements are in good agreement and support this assignment. From flow experiments, Ag-ZSM-5 catalysts showed a two-fold increase in selectivity towards benzene, toluene and xylene (BTX) in comparison to H-ZSM-5 at comparable ethylene conversions. DFT calculations suggest that the two types of acid sites in the zeolite – Brønsted (H^+) and Lewis (Ag^+) have distinct functions. Initial ethylene activation and subsequent oligomerization occur at the H^+ sites with moderate activation barriers. Transient kinetics experiments strengthen these assertions, with butene, propane and hydrogen gas being detected at the reactor exit. Through simulations, Ag^+ sites exhibit strong binding to ethylene and higher olefins, while being unable to activate ethylene due to large activation barriers. Ag^+ behaves as an olefin aggregator and provides facile pathways to form cyclic species. Aggregation of olefins and accelerated aromatic species and hydrogen production is again confirmed through transient kinetics experiments in which no butene is detected at the reactor outlet. Furthermore, product selectivity trends are consistent with those obtained from flow experiments in which the highest BTX selectivity was observed for an Ag loading (Ag/Al) of 0.08. Overall, our studies help distinguish between the activity and interplay between two types of active sites in a metal-exchanged zeolite and in-turn provide a basis for structure-function relationships that will aid in catalyst optimization.

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9. Role of the Metal Support Interface in H₂ Activation on Supported Gold Nanoparticles

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Global hydrogen production exceeds 50 million tons per year, largely for the production of ammonia. Given its importance, a fundamental understanding of hydrogen activation is vital when designing new catalysts. Hydrogen is traditionally thought to proceed through a homolytic activation mechanism over late transition metals. For supported Au catalysts, the homolytic H₂ activation was proposed to occur at the interface supported Au clusters.¹ In the last ~5 years researchers have investigated heterolytic pathways for H₂ activation.² Guoxiang *et al.* found that a heterolytic pathway for hydrogen cleavage was kinetically favored over Au/TiO₂.³ Our group also published experimental and DFT evidence that supports a heterolytic H₂ activation mechanism at the Au-TiO₂ interface.⁴

In this study, we probe the thermodynamic properties of hydrogen oxidation with a Van't Hoff analysis over Au/MO_x. From the Van't Hoff plot we derived the enthalpy and entropy terms for H₂ oxidation. For Au/TiO₂, the enthalpy and entropy values are $-23 \pm 5 \text{ kJ}\cdot\text{mol}^{-1}$ and $-50 \pm 10 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ respectively. These values represent a significant reduction from other metals supported on an alumina base, suggesting a different reaction pathway for gold nanoparticles. For example, rhodium on alumina gives enthalpy and entropy values of $-100 \text{ kJ}\cdot\text{mol}^{-1}$ and $-160 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ respectively.⁵ The differing thermodynamic values suggest a different mechanistic pathway for hydrogen activation on gold.

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10. Impact of copper exchange protocol on Cu-CHA SCR activity

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One of the major milestones in environmental catalysis is the abatement of environmentally harmful compounds such as hydrocarbons, nitrogen oxides (NO_x), sulfur oxides (SO_x) and carbon monoxide, produced by automobiles and power sources. The discovery of Cu-CHA as a catalyst for selective catalytic reduction (SCR) of NO_x was a breakthrough and led to a rapid commercialization of the technology for the “lean-NO_x” emissions control. It is a relatively new technology and requires more research on identification of active sites of the catalyst in order to develop next generation catalysts with improved performance, enhanced stability and low cost.

There have been considerable research and progress in molecular-level understanding of the nature of active Cu species and the SCR reaction mechanisms. Unfortunately, many studies were conducted using Cu-CHA prepared via different synthesis methods. Current work investigated four methods of preparation of copper exchanged zeolites reported in the literature and the NO_x SCR activities were examined using a packed bed flow system. The SCR activities of each sample were considerably different at lower temperature that is relevant to the “lean-burn” engine operational temperature. The differences between catalysts prepared via different protocols were further studied by CO binding experiments where it was revealed that each protocol results in different copper species within the zeolite framework. DFT calculations were coupled with CO binding and catalytic results to identify active sites. The poster will show synthesis, characterization and catalytic testing details and results.

11. Not all hydrogens are created equal: Theoretical and experimental insight into how protons and hydrides steer different hydrogenation rates for alkynes and O₂ over Au/TiO₂

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Preferential oxidation of CO (CO PrOx) and selective alkyne hydrogenation are two industrially important processes involving H₂ in their feed streams. CO PrOx is potentially useful for purifying hydrogen streams from methane steam reforming, due to its improved energy efficiency relative to methanation. Recent studies have shown that the selectivity of Au catalysts towards CO oxidation can be enhanced by poisoning the H₂ activation sites at the metal-support interface (MSI).^(1,2) Selective hydrogenation of alkynes in polyolefin feedstocks to alkenes is an important step in the plastics industry to prevent deactivation of the downstream polymerization catalyst. Both reactions are generally considered to be hydrogen coverage limited; however we have observed significantly lower reaction rates for 1-octyne hydrogenation (relative to H₂ oxidation) on the same Au/TiO₂ catalyst.

We explain this phenomena with the help of density functional theory (DFT) calculations. The DFT calculations show heterolytic H₂ activation at the MSI, which results in a support proton and a formal gold hydride, is the most energetically favorable pathway for H₂ activation on Au/TiO₂. The gold hydrides generated by H₂ activation near the interface were shown to be less stable than the support protons, thus resulting in a spillover to the support.⁽²⁾ Thus the H₂ activation near the interface, either homolytically on just gold sites or heterolytically across the interface would lead to spillover of gold hydrides onto the support resulting in low hydride coverage on gold. The addition of support protons to O₂ is facile, facilitating the use of protons generated by H₂ activation near the interface. Whereas in the case of alkyne hydrogenation, the calculated barriers for proton addition to propyne are twice those of the barriers for hydride addition, suggesting that the hydride addition is the preferred pathway for alkyne hydrogenation. Thus, H₂ activation near the interface which results in support protons because of spillover does not help the alkyne hydrogenation. The relatively strong binding reported for 1-octyne to the support and the Au/TiO₂ interface is also one of the factors that likely limits the role of the interface sites as active sites for hydrogen activation during alkyne hydrogenation.⁽³⁾ To verify the DFT predictions we performed a particle size study, where we measured the H₂ oxidation and 1-octyne hydrogenation rates on catalysts with different gold particle sizes. For 1-octyne hydrogenation, the turnover frequencies (TOF) were the same between different particle sizes when they were based on surface sites. While for H₂ oxidation, the TOF were the same when they were based on perimeter sites. This is in agreement with the predictions from DFT that the surface gold sites are the active sites for 1-Octyne hydrogenation and the Au/TiO₂ interface sites are the active sites for O₂ hydrogenation.

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12. Molten Salt Synthesis (MSS) of MgO(111): Critical Factors Governing the Crystallization Process

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In metal oxide catalysis, the performance of the catalyst often depends on the exposed crystal facets. Suitable strategies for controlling the faceting of metal oxide crystals are therefore needed. The generation of high index facets, such as {111} surfaces, is often desirable given the large number of undercoordinated metal sites that are available for catalytic reactions. Here we discuss the ability to stabilize these facets during the synthesis of MgO crystals. For instance, MgO(111) preparation has been shown to be attainable by molten salt synthesis (MSS);¹ however, the main driving force(s) and factors that determine the particles morphology have largely remained elusive. In this work,² we examine the thermal decomposition of different MgO precursors to assess the influence of precursor decomposition pathways in the formation of octahedral MgO particles. We found that solid-to-solid conversions and recrystallizations in molten nitrates or chlorides are usually incapable of producing well-defined octahedral MgO, indicating that ion adsorption on MgO (and facet stabilization) may not be the main morphological driving force. We show for $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, the most suited MgO(111) precursor, that its decomposition trajectory is crucial in determining the exposure of {111} facets. For neat $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ decomposition, MgO{111} facets are promoted via magnesium nitrate intermediates in the molten state and in the presence of residual water. In molten $\text{NaNO}_3:\text{KNO}_3$, the formation of liquid eutectic mixtures facilitate H_2O retention and ionic mobility, from which well-defined octahedral MgO crystals form, thereby emphasizing the crucial role of water in Mg(II)-nitrate systems. In a NaCl:KCl ionic medium, MgO(111) crystallization occurs via a molten $\text{K}_3\text{NaMgCl}_6$ intermediate in which the H_2O content is negligible. In summary, the formation of polar MgO(111) particles is facilitated in molten salt media when MgO is generated via a liquid-to-solid reaction (with intermediates in the molten state). The presence of residual water and ions impact MgO(111) crystallization in ways that still remain elusive, but are not necessarily governed by adsorption-stabilization processes.

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13. Computational Study of Carbonate Assisted Electrochemical Methane Activation on Ni(111) and NiO(100) Using Density Functional Theory

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Methane, an abundant resource in the U.S., 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 challenging but very desirable. Two major issues that current catalysts are facing are that high temperatures (up to 900 K) are required¹, and the life time of the catalysts is limited by sintering and coking². Inspired by the work of Spinner and Mustain³, 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 deliver a single oxygen atom that 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. The rate of CO_3^{2-} delivery can be controlled by adjusting the cell potential and current density. By simultaneously controlling the concentration of CH_4 at the anode, we anticipate that the over-oxidation of methane can be prevented, such that a high yield of methanol can be achieved.

To obtain fundamental insights into the feasibility of such process, we have performed density functional theory (DFT) calculations on Ni(111) and NiO(100) in VASP and explicitly accounted for the effects of applied electric fields. Our results indicate that the interaction between the externally applied electric field and the dipole moment generated between the surface and adsorbates plays the dominant role in altering the binding behavior; the same external electric field may stabilize some adsorbates, while destabilizing others, depending on the orientation of their respective dipole moments. Hence, the reaction enthalpy and activation energy of certain elementary steps exhibit a strong dependence on the applied electric field. Although an applied electric field does not significantly lower the methane activation barrier on Ni(111), 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. Strong Lewis Acid-Base interaction has been observed on NiO(100) during the calculations, and careful interpretation of the results is needed before making any conclusion for NiO(100).

While the development of a viable process remains in its early stages, our results suggest that an electrochemical cell with a tunable electric field offers unique advantages for selectively upgrading methane to value-added products.

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14. First-principles Kinetic Monte Carlo Study of Biomass Conversion over Titania Supported Ruthenium Catalyst

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Catalytic upgrade of bio-oil to fuels and chemicals requires the selective reduction of its 10-40 wt% oxygen content.¹ Ruthenium supported on titania (Ru/TiO₂) has recently evolved as one of the better performing catalysts for such hydrodeoxygenation (HDO) processes. Commonly proposed HDO mechanisms on oxide containing materials invoke oxygen vacancy sites as catalytically active sites, but the mechanism of their formation remains disputed.

To address this question, we use first-principles kinetic Monte Carlo (kMC) simulations to investigate the HDO reaction of *m*-cresol over TiO₂(110) in the presence and absence of Ru, with particular focus on the Ru/TiO₂ interface. To eliminate the strong effect of Lewis acid-base pairs on adsorbate-adsorbate interactions as illustrated by Metiu *et al.*², we extract pairwise interaction parameters from a series of co-adsorbed configurations that do not exhibit any electronic artifacts on rutile TiO₂(110). Our kMC results show that the presence of Ru nanoparticles substantially increases the reduction rate of the TiO₂(110) surface attributed to H spillover and a facile, heterolytic H₂ cleavage pathway across the Ru/TiO₂ interface. We also qualitatively reproduce experimental results for water adsorption on TiO₂(110).³ Under HDO reaction conditions over Ru/TiO₂, the Arrhenius plot exhibits two kinetic regimes at low and high temperatures, corresponding to a coverage transition occurring at around 550 K. The presence of added water in the feed impedes this reaction pathway through vacancies by rapid water dissociation on vacancies, resulting in two hydroxyl groups. Alternatively, we propose proton-assisted HDO reactions occurring at the interface.

Overall, our detailed simulation is capable of capturing coverage effects and mechanistic changes in response to variations in temperature or feed composition, including the addition of water to the feed. To our knowledge, there exists no comparable model with the ability to discriminate between metal, oxide and interfacial activity, and assign a dominant catalytic role to each component. The ability to generate such detailed fundamental insight can be leveraged for the future design of multifunctional catalysts with unprecedented selectivity advantages.

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15. Dual Role of Surfactants in Zeolite Synthesis and Catalyst Optimization

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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 efforts 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 cationic surfactant cetyltrimethylammonium (CTA) as an organic structure-directing agent (OSDA) and as a mesostructuring agent in the rational 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.² In ZSM-5 synthesis it is challenging to identify new and inexpensive OSDAs that can tailor the physicochemical properties of the final product. The most frequently used OSDA in ZSM-5 synthesis is tetrapropylammonium (TPA); however, recent studies have shown that CTA can be used as an alternative.^{3,4} Here, we will present the effects of using CTA and TPA as OSDAs in combination with a variety of alkali metals as inorganic structure-directing agents. Our findings reveal that the selection of inorganic/organic 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 structure-directing agents 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 OSDA 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 OSDA design, the development of mesoporosity in zeolites has been a long-standing goal in catalysis to alleviate the diffusion limitations imposed by micropores.^{5,6} One area of research that has garnered considerable interest, yet is not fully understood, is the rearrangement of zeolite crystals post-synthesis 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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16. A Three-step Reaction to Produce Fuel from Oxygenates via Multifunctional Catalysts

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Sustainably meeting the growing energy needs of the planet is one of the 21st century's grand challenges. Global energy demand will increase nearly 60% in the next 25 years. Many pathways to meeting our energy needs while reducing fossil-fuel consumption have been posited, all with challenges. One possible route is to convert biomass into fuels.

In this work, we designed a three-step process that includes hydrogenation of phenol, aldol condensation, and hydrogenation of aldol reaction product to produce fuels from oxygenates using palladium containing dendrons supported on ordered mesoporous silica (OMS). Palladium/dendron-OMS catalyzes the phenol hydrogenation and hydrogenation of aldol coupling products while dendron-OMS without Pd was used for the aldol condensation. 85% yield of cyclohexanone was obtained in the first step (phenol hydrogenation). It is also shown that several aldehydes can be used in Aldol reactions with cyclohexanone, including 4-nitrobenzaldehyde (4-NBA), hydroxymethylfurfural (5-HMF) and benzaldehyde (BA). The aldol products were hydrogenated using Pd/dendron-OMS yielding products not dissimilar from what one observes from aqueous phase reforming (APR). The operating conditions of low temperature and low pressure hydrogen in aqueous media is consistent with green chemistry goals.



17. Dirhodium Tetrphosphine Hydroformylation Catalysts: Bimetallic Cooperativity

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Bimetallic cooperativity can potentially increase activity of reactions. This concept is another way to increase reactivity besides simply focusing on the steric and electronic effects of a ligand. A binucleating tetrasphosphine ligand has been developed to showcase bimetallic cooperativity between two rhodium metal centers. Hydroformylation is a widely used industrial process to produce aldehydes from alkenes, H₂, and CO. The dirhodium catalyst, [Rh₂(μ-CO)(CO)₃(*rac*-et,ph-P4-Ph)](BF₄)₂, is highly active leading to favorable results when using a DMF/water solvent system, 1-hexene, 90 psi 1:1 H₂/CO, and 90° C: initial turnover frequency of 35.4 min⁻¹, linear to branch ratio of 17.6:1, isomerization of 1.9% alkene isomerization, and hydrogenation of < 1%. Unfortunately, this complex was very difficult to make from our usual catalyst starting material, [Rh₂(nbd)₂(*rac*-et,ph-P4-P4)](BF₄)₂ (nbd = norbornadiene).

My research has focused on the synthesis and optimization of the new dirhodium-tetraphosphine catalyst precursors. New catalyst precursors with acetonitrile, pyridine, and cyclooctadiene ligands demonstrate high activity for hydroformylation in water/acetone solvent with results displaying high turnover numbers ranging from 700-800 aldehyde turnovers and low side reactions (alkene isomerization = 5% -7%, hydrogenation = >1%) point to an effective catalyst. The chelator effect of the phenyl linkage ultimately became an issue for stability of the catalyst. The new P4-Ph tetraphosphine ligand, however, has internal phosphines with two P-aryl bonds and only one alkyl group (the central methylene bridge). These are considerably more reactive towards P-aryl group cleavage reactions that leading to rhodium-induced P4-Ph fragmentation. *In-situ* FT-IR and NMR experiments were performed on the bimetallic catalyst to understand the active catalyst and mechanism for the catalytic cycle.



18. Characterization of Two-metal Zeolites: Cu/Zn-ZSM-5 as a Catalyst in the Partial Oxidation of Methane to Methanol

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The zeolite family of minerals contains hundreds of microporous materials, many of which have become valuable catalysts for industry and research. Discovered and patented by Mobil Oil in the mid-1970's, the aluminosilicate zeolite ZSM-5 (of the MFI structural family) has found widespread use in fluidized catalytic cracking (FCC), hydrotreating, and methanol-to-gasoline (MTG) technologies. Ordered pentasil groups delimit parallel straight-channel pores normal to intersecting sinusoidal pores of diffusible diameter 4.7Å, yielding an extremely high surface area-to-mass ratio on the order of 270 m²/g. Aluminum substitutions into the siliceous framework disrupt the local charge neutrality, requiring a cationic counterion at distinct Z sites to satisfy neutrality. The ability to exchange a range of cations, including monovalent and divalent d-block metals, into these Z sites imparts a diverse field of possible modifications. The catalytic properties of ZSM-5 are determined primarily by the demographics of the counter-ion population. About thirty years of research has yielded much literature on single d-block metal substitutions, with little advancement into more complicated systems. This work investigates the spectroscopic and catalytic behavior of MFI structures containing more than one d-block metal. Presented material introduces synthetic techniques and exchanges for Cu and Zn guest ions as well as early research into the series exchange of a dual-metal derivative. The catalytic potential of these species is evaluated in a model reaction: the partial oxidation of methane.



19. Functionalized OMS as Model Materials for Cellulose Depolymerization Products Capture

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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. By grafting amine functional groups on high-surface area supports, 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. To gain a macroscopic understanding of the binding process, 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. Results showed that primary and quaternary amines had the highest uptake with uptake values for both equal to 0.21 mmol acetic acid/g OMS. Additionally, uptake was shown to significantly decrease for all amines with increasing salt concentration and a significant decrease in uptake was observed with increasing pH. Competing uptake of varying alkyl chain length organic acids was also tested and it was found that the most hydrophobic acid was preferentially bonded to the grafted amine groups. These results show that the nature of the amine is an important parameter for acid separations and it is likely to have implications for base-catalyzed reactions and metal ion-amine chelation.

For the next phase of the work, aromatic ligands with varying chemical properties were grafted on OMS supports to determine the crucial parameters for extracting aromatic cellulose depolymerization products. Guaiacol was initially chosen as the model aromatic chemical to be extracted due to its chemical properties and potential industrial relevance. High and uniform loading of ligands was found to be difficult to obtain due to the bulk of the aromatic groups and crowding at the OMS pore opening, and to avoid these issues dendritic structures were synthesized to ensure uniform loading while obtaining higher ligand density. The guaiacol uptake results showed that hydrophobicity was the crucial parameter for the separation and mixed systems of aromatic extracts were then compared to obtain a full picture of the uptake process. Additionally, very high-ligand density ligands were synthesized in an attempt to obtain the highest selective uptake possible.

20. Enhanced Surface Activity of MWW Zeolite Nanosheets Prepared by a One-Step Synthesis Method

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Zeolites are shape-selective microporous crystals that have been widely used as heterogeneous catalysts in petroleum and chemical industries.[1] However, pore dimensions (4-7 Å) of typical zeolites would often encounter diffusion limitation especially in applications that involve bulky molecules. MCM-22 (MWW type) zeolite exhibits properties that improve mass transport by providing accessible acid sites on or near its external surface.[2] Conventional layered MCM-22 precursors lead to the direct condensation of MWW layers during calcination, sacrificing significant accessibility to surface acid sites. In our studies, we have demonstrated a novel approach to obtain disordered MWW-type material with high external surface acid sites via a commercially-viable single step protocol.

Disordered MCM-22 was obtained in a one-pot synthesis using a quaternary ammonium modifier to disrupt the natural alignment of MWW layers. A series of catalysts were prepared with varying Si/Al and a range of layer disorder to assess the degree of impact of external surface area on catalytic performance. Electron micrographs reveal stark differences in the morphology and thickness of ordered and disordered zeolites. The packing structure of MWW materials and their interlayer distances can be identified from powder XRD patterns in the range $2\theta = 6-10^\circ$. The degree of disorder was quantified by the disorder index, which is defined as the ratio between external and total surface areas (varying from 0.3 to 0.7 for ordered and disordered materials, respectively). The impact of modifiers on Al incorporation into disordered MWW materials was explored by solid state ²⁷Al NMR measurements and by varying the synthesis gel Si/Al ratio. We observe notable differences in the locations of Al at tetrahedral sites in the frameworks of ordered and disordered MWW samples. This study provides a novel approach for the one-pot synthesis of disordered MWW with high surface area and tunable Al density and siting. The ability to selectively tailor the physicochemical properties of zeolites allows for the development structure-performance relationships.

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21. Core-Shell Pt/Al₂O₃@Cu-ZSM-5 catalyst for Selective NH₃ oxidation

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The Ammonia slip catalyst (ASC) is an essential after-treatment unit in modern diesel vehicles. The purpose of ASC is to prevent the release of unreacted NH₃ leaving from upstream Selective catalytic reduction (SCR) unit. The state-of-the-art ASC for selective oxidation of NH₃ to N₂ has a dual-layer architecture with a Pt/Al₂O₃ bottom layer (PGM) and a Cu/Fe-exchanged zeolitic (M-Z) top layer¹. The dual-layer structure helps to improve the N₂ selectivity at high NH₃ conversion. While recent studies demonstrate the effectiveness of the dual layer design², further advances are needed to reduce the PGM loading and ASC volume while enhancing low temperature activity.

In this work, the dual-layer concept is scaled down to the level of a single catalyst particle. A core-shell (CS) particle comprising a PGM core and M-Z shell; specifically, Pt/Al₂O₃@Cu/ZSM-5 was synthesized. Synthesis involved seeding of the core followed by secondary growth for ZSM-5 shell coverage³. Reaction testing of CS catalyst in fixed-bed showed enhanced low temperature activity for NH₃ conversion with high N₂ selectivity (yield ~ 90 %). The NO_x yield was below 10 % even at high temperature of 500°C. On comparing with a physically mixed [Pt/Al₂O₃ + Cu/ZSM-5] catalyst having same Pt & Cu loading, the maximum N₂ yield achieved was ~ 50 % which dropped to ~40 % at 500°C. The high selectivity for CS catalyst is due to the presence of Cu-ZSM-5 shell where SCR chemistry takes place².

Notably, for similar Pt loading of 0.05 wt %, light off for CS catalyst (250°C) was 60°C lower than Pt/Al₂O₃ (310°C) which was comparable to the light-off of Pt/Al₂O₃ (260°C) catalyst having 3x Pt loading. Reaction testing for steady state ammonia oxidation over different stages of synthesis (core→seeded core→CS). The seeded core had a light off at 215°C, which is 95°C lower than Pt(0.05)/Al₂O₃. The CS catalyst with fully developed shell of ZSM-5 lowered the light off to 250°C due to the diffusion resistance which is still lower than Pt(0.05)/Al₂O₃. The enhanced activity was due to the de-stabilization of platinum oxide exposing the more active metallic platinum in CS catalyst. The destabilization effect was related to the change in metal-support interactions supported by H₂-Temperature programmed reduction (H₂-TPR) experiment^{4,5,6}. These findings not only confirm that the dual-layer ASC concept can be achieved at the single particle level, but there is an apparent added advantage of lower light-off at reduced PGM loading not obtained previously.

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22. 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 A 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 FAU crystallization which has only been observed to crystallize by non-classical pathways.

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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23. Experimental and Modeling Study of Passive NO_x Adsorbers: Pd-H-ZSM-5

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With the announcement by the Environmental Protection Agency (EPA) to impose more stringent regulations for emissions of NO_x (NO+NO₂) with a target-year implementation of 2024, reduction of NO_x emissions has become a great challenge for the vehicle industry. Advanced technologies like selective catalytic reduction (SCR) and NO_x storage and reduction (NSR) have been implemented for NO_x reduction in diesel and lean gasoline emission control. However, their effectiveness at temperatures below 200°C is limited. Thus, NO_x emissions during the vehicle cold-start complicate the meeting of the aforementioned emission rules. The passive NO_x adsorber (PNA) has emerged as a solution to reduce NO_x through capture and conversion of NO_x emitted during a vehicle's cold-start period. Pd impregnated on zeolites (ZSM-5, BEA and SSZ-13) can adsorb NO at temperatures below 100°C and release NO+NO₂ at temperatures above 200°C, enabling their reduction by downstream SCR or NSR. There is a need for mechanistic-based PNA kinetic and reactor models to identify improved materials and to develop effective trapping strategies. A combined experimental and modeling study was conducted to understand and predict the effects of various operating parameters on a model PNA material: Pd-H-ZSM-5. Specifically, the effects of temperature, flowrate, Pd-loading, O₂, and H₂O were investigated and used to develop a predictive reactor model.

Typical NO_x uptake data revealed the process to be kinetically limited and to not be washcoat diffusion limited. Water was shown to significantly lower NO_x uptake, but the extent of inhibition is a strong function of temperature. Typical NO uptake in the presence of H₂O in the feed did not exceed ~0.4 NO/Pd indicating that most of the Pd was not in cationic form. A transient monolith model for NO_x uptake and TPD was developed for H-ZSM-5 and Pd-H-ZSM-5 with and without H₂O in the feed. Initial model parameters for the reaction network were obtained from DFT calculations and subsequently tuned to capture the spatiotemporal features of the passive NO_x trap. The model assumes that the dispersed Pd cations that are Z⁺[Pd(II)OH], Z⁺Pd, Z⁺ and Z⁺Pd, are the active sites for NO_x adsorption together with the Brønsted sites in Pd-H-ZSM-5, the latter of which are ineffective when water is present in the feed. The model was validated for different uptake temperatures, feed flow rates and Pd-loadings, affording its use to identify the optimal catalyst formulation as well as operating strategy.

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24. Effects of Mn on CO Adsorption and Carbon Deposition on Co(poly)

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The addition of Manganese to Cobalt based Fischer-Tropsch catalysts has been shown to tailor products to short chain hydrocarbons, long chain hydrocarbons, and long chain alcohols.¹⁻³ While these phenomena have been studied on high surface area catalysts, little work has been performed on Mn/Co systems in Ultra-High Vacuum (UHV) for the Fischer - Tropsch reaction. By depositing sub-monolayer metallic Mn onto a Co polycrystalline foil via Electron-Beam Evaporation in UHV, we were able to study CO adsorption and carbon deposition. King and Wells experiments at 77 K showed that Mn decreased CO uptake while simultaneously promoting dissociative adsorption of CO. By using Auger Electron Spectroscopy (AES), we were able to study carbon deposition before and after reaction in a batch reactor setup. It was seen that 0.25 ML Mn on Co(poly) decreased carbon deposition after reaction in a 1:4 CO:H₂ mixture when compared to clean Co(poly) foil.



25. Computational Exploration of Selective Ethylene Dimerization over Hydrogenation on Iridium Doped NU-1000, Al-NU-1000 and UiO-66

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The favorable structural features of metal-organic frameworks (MOFs) namely high porosity, broad chemical diversity, tailorable pores have sparked a great interest in their usage for many applications including catalysis, gas capture and separation etc. The tunability of these structures has recently been utilized to dope metal complexes on them by the synthetic methods of atomic layer deposition and solvothermal deposition.

Among the large set of MOFs, particularly, Zr-based MOFs have been attractive for experimental studies as they maintain their stability under harsh experimental conditions ascribed to potent Zr-O bonds. This computational work focuses on the ethylene dimerization and hydrogenation mechanisms on Ir(C₂H₄)₂H₂ loaded NU-1000, Al-NU-1000 and UiO-66 MOFs utilizing density functional theory (DFT) calculations on cluster models. The cluster models are based on the DFT optimized periodic models of MOFs where organic linkers are shortened to acetate groups. Several reaction mechanisms are characterized and their activation barriers are contrasted to determine the reaction paths that are more likely to be followed. The relative difference between the activation barriers of ethylene dimerization and hydrogenation mechanisms is assessed to explain the experimental selectivity trends. The similarity between DFT models and experimental structures is evaluated by comparing the computed interatomic distances and those obtained by EXAFS measurements.



26. Reduced-Order Models with Local Property Dependent Transfer Coefficients for Real Time Simulation of Monolith Reactors

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The monolith reactor is the most widely used reactor in catalytic after-treatment systems (e.g. TWC, DOC, LNT, etc). The detailed mathematical models of a monolith reactor consist of a system of coupled nonlinear partial differential equations (PDEs) in at least two spatial dimensions (axial and radial/transverse) and time along with highly nonlinear source/sink terms appearing in the solid (catalyst) phase species and energy balances. Although the numerical solution of such detailed models with complex catalytic chemistry is possible with the present day computers, it may be demanding in terms of time and memory requirements, especially for real time simulations that may be needed in the control and optimization schemes. Therefore, the development of low-dimensional (reduced order) models for these systems is important for various control and optimization algorithms related to fuel economy and real time implementation of emissions constraints. There are several simplified approaches proposed in the literature for the solution of diffusion-reaction equations in the washcoat to avoid the computational demand of the full numerical solution.

We present and evaluate the accuracy of these simplified approaches for reduced order models and a new approach with local property dependent internal and external transfer coefficients for real time simulation of monolith reactors. We illustrate the application of the models to three-way catalytic converters (TWCs) with a single washcoat layer to determine the steady-state as well as transient behavior in real time. We also compare the solutions obtained using reduced order models with detailed model to assess the accuracy. We show that use of local property dependent transfer coefficients in terms of the Jacobian of reaction rate vector leads to the best match followed by its diagonal approximation followed by the asymptotic values, especially in the washcoat diffusion controlled regime.

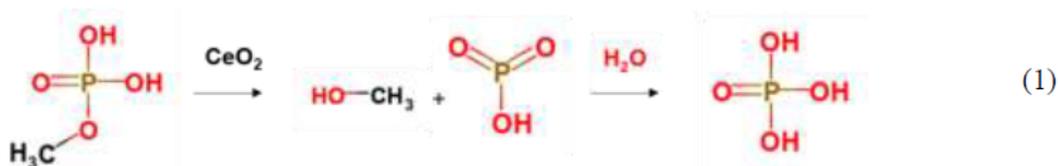
27. Computational study of dephosphorylation on CeO₂(111) catalyst surface

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The ability of ceria to catalyze phosphate ester bond cleavage has been shown experimentally,¹ to decontaminate excess organophosphates accumulated in water bodies from agricultural runoff, industrial or municipal waste water discharges. We have employed first principles density functional theory calculations to study the catalytic dephosphorylation of model organic monophosphates, methyl phosphate, para-nitrophenyl phosphate, and phosphoric acid, on the thermodynamically most stable facet of ceria, CeO₂(111). Bonding of phosphorous atom to the lattice oxygen is energetically most preferred, over the weak interaction of phosphoryl oxygen with Ce⁴⁺ on the stoichiometric ceria surface. Partial reduction of ceria surface does not lower the energy required for adsorption of monophosphates. In the surface assisted reaction pathway, adsorbed phosphate monoesters undergo P-O ester bond scission, leading to the formation of an alcohol and HPO₃. Hydration of HPO₃ for subsequent desorption as H₃PO₄, are found to be rate-limiting for reaction in vacuum,² with the example of methyl phosphate shown in Eq. (1). Inclusion of solvation, pH, and coverage effects on this system is expected to provide more reliable energy barriers, that can be analyzed to devise an economical process for removal and recovery of phosphorous from waste water.



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28. Direct Z-Scheme Charge Transfer in MoO₃/g-C₃N₄ hybrid Photocatalysts and the Generation of Active Radicals in Photocatalytic Dye Degradations

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Photocatalytic degradation is an attractive strategy to purify waste water contaminated by macromolecular organics. Compared with the single-component photocatalysts, heterostructures of different semiconductors have been widely used to improve the photocatalytic performance. In this work, we fabricate a hetero-structured photocatalyst consisting of two-dimensional graphitic carbon nitride (g-C₃N₄) nanosheets and commercial MoO₃ microparticles through a simple mixing and annealing process. The photocatalytic performance is evaluated in various dye degradation reactions. The MoO₃/g-C₃N₄ composite shows a significant improvement compared with individual MoO₃ or g-C₃N₄ as well as their physical mixture. By applying electron spin resonance (ESR) spin-trap spectra, radical scavenge experiments and electrochemical analysis, we find that a direct Z-scheme charge transfer between MoO₃ and g-C₃N₄ not only causes an accumulation of electrons in g-C₃N₄ and holes in MoO₃, but also boosts the formation of superoxide radical and hydroxyl radical. The superoxide radical and hole dominate the photocatalytic degradation, while the hydroxyl radical plays a negligible role and its production can be suppressed by lowering the pH value.



29. Autothermal Operation of Catalytic Oxidative Coupling of Methane in Packed-Bed Reactors

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Oxidative coupling of methane (OCM) is an attractive route for the direct conversion of methane into value added chemicals. The highly exothermic feature of OCM system leads to complex ignition-extinction behavior that depends on both operating conditions and design parameters. Experimentally observed hysteresis behavior in lab-scale reactors motivated the investigation of the feasibility of autothermal operation for OCM. In steady-state autothermal operation, there is no heat addition to the reactor and there is no intentional heat removal by cooling through reactor walls. The existence of multiple steady-states, and in particular an ignited high temperature (conversion) state is essential for autothermal operation with low feed temperatures or space times. High temperature ignited steady-state can be attained either by reactor scale back-mixing of heat or by interphase gradients leading to particle level ignition. The present work examines the impact of operating variables (space time, methane to oxygen ratio and feed temperature), inter and intra-phase gradients and bed level heat and mass dispersion on the ignition-extinction behavior and C₂ product selectivity in catalytic OCM reactors.



30. Support Effects for the Selective Hydrogenation of 1-Octyne over Au/MO_x

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The selective hydrogenation of alkynes into alkenes is a vital reaction to the polymer industry. Polyolefin feedstocks, such as ethylene or propylene typically contain ~2-5% alkyne impurities. This concentration must be less than 10 ppm to avoid poisoning the downstream polymerization catalysts. Currently, Pd-based catalysts are used to selectively convert alkynes into alkenes. However, Pd itself will over-hydrogenate and convert the majority-olefin feed into alkanes; deactivation also occurs through the formation of oligomers (“green oil”). Gold catalysts are a promising alternative to Pd due to weak ethylene binding that results in a greater selectivity. However, Au deactivates within a few days and requires process temperatures > 200 °C. This study quantifies how the electronic modification to interface Au atoms by the MO_x support affect the rate of alkyne hydrogenation.

Supported Au catalysts were synthesized through a colloidal method to ensure consistent Au particle sizes. Supports included Al₂O₃, TiO₂, and SiO₂. Initial activity was measured with lightoff curves for the hydrogenation of 1-octyne, an analog for acetylene. Kinetic parameters (E_{app} , 1-octyne order, H₂ order) were also determined. The results for all of the catalysts were nearly identical, suggesting that the electronic effects from the support are kinetically negligible. *In-situ* alkyne adsorption experiments and DFT simulations show significant alkyne adsorption on interface Au NP’s and hydroxylated support sites. The mechanism most consistent with our kinetic data includes the non-competitive activated adsorption of H₂. The adsorption of 1-octyne was observed via FTIR for selected catalysts.

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31. NO Oxidation in Brønsted Acidic Chabazite within Low and High Temperature Regimes: A Theoretical Study

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Nitrogen Oxides (NO_x) are common toxic pollutants that are produced during high temperature oxidation, for example, in combustion engines. Catalytic NO_x reduction by ammonia in metal-exchanged zeolites is a well-established method to convert these contaminants into environment-friendly species (N₂ and H₂O).¹ Equimolar mixtures of NO/NO₂ are desirable, because they can undergo the most effective fast NO_x reduction reaction;² yet, combustion processes typically produce more NO than NO₂. Therefore, NO oxidation is a relevant step prior to NO_x reduction and has been extensively studied. While NO oxidation may occur uncatalyzed as homogenous reaction, it has been shown that confinement and entropic effects in small pore zeolites increase the oxidation rate, with SSZ-13 demonstrating the best performance.³ When heterogeneously catalyzed over acidic zeolites, NO oxidation at low temperature (263-473 K) is unusual because its rate decreases with increasing temperature, resulting in a negative apparent activation barrier.^{3,4} At high temperature (> 473 K), however, rate increases with increasing temperature.⁵ In this contribution, we use density functional theory (DFT) to shed some light on this puzzling observation and investigate the mechanistic differences at low and high temperature.

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32. 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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33. NiAu Catalysts for the Selective Hydrogenation of Terminal Alkynes

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In a recent paper, we used a colloidal synthesis method to generate Au NP's in solution and then deposited them on a variety of metal oxide supports.¹ These catalysts were used to quantitatively evaluate the electronic support effects during selective alkyne hydrogenation. We found that the choice of support did not significantly affect the rate of hydrogenation despite controlling for particle size. Therefore, we sought to tune the activity of Au by adding Ni. In this work, we extended the synthesis to include the generation of colloidal Ni NP's.² The surface Ni atoms were subsequently exchanged with Au through galvanic deposition and then immobilized on an Al₂O₃ support.

Three NiAu catalysts were tested against a colloidal Ni catalyst (c-Ni), c-Au, industrial Au and Ni catalysts, and c-Au/NiO for the selective hydrogenation of 1-octyne. The selectivity of Ni catalysts to 1-octene, determined by light-off curves, was generally poor with relatively narrow temperature windows for optimal 1-octene yield (~10 °C). However, all bimetallic catalysts saw large increases in 1-octene selectivity with optimal yields spanning over 100 °C, a great improvement over both Ni and Au catalysts. The apparent rate constant of monometallic Ni was at least 10 times higher than Au; the bimetallics were 2-3 times higher than Au, but the kinetics were otherwise very similar between all catalysts. The catalyst surface is likely a mixture of Au covering Ni with some exposed Ni.

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34. Physisorbed H₂O on Metal-Oxide Supported Au Nanoparticles: Origin of Poisoning Effect in H₂ Oxidation

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Global annual demand for H₂ has risen to over 50 million tons and is expected to grow to a \$150 billion industry by 2022.^{1,2} H₂ is used in methanol synthesis, petroleum refining, electronics, food processing and ammonia synthesis, which consumes 2% of the global energy consumption. H₂ is primarily produced through steam reforming natural gas, and after the water-gas shift reaction, a ~1% CO impurity is present, which must be removed for a number of the above processes. Preferential Oxidation (PrOx) shows promise as a potential alternative to methanation and pressure-swing adsorption, which have operating and capital limitations. Recently, while studying H₂ oxidation, the undesired side reaction of PrOx, over supported Au catalysts, we proposed a heterolytic H₂ activation mechanism that occurred at the metal-support interface (MSI) which was strongly inhibited by physisorbed H₂O.³ The current study aimed to expand on the mechanism of poisoning by H₂O, as this has shown to be an issue in other systems also.

We used steady-state reaction kinetics, spectroscopy and DFT calculations to elucidate how H₂O inhibits H₂ oxidation over commercial Au/TiO₂. We measured the H₂ oxidation apparent activation barrier, E_{app}, at constant feed H₂O pressure and observed that E_{app}, changed substantially when the pressure of H₂O was varied. This revealed two distinct kinetic regimes; H₂O coverage less than 1 monolayer equivalent (MLE) (with support hydroxyls exposed) and greater than 1 MLE (no available MSI sites). The energetics of the elementary steps were calculated and showed that our previously reported mechanism was largely consistent, but that all steps were slower, H₂ activation whose barrier increased by a factor of 2. We re-measured the E_{app} values with constant H₂O coverage (using BET adsorption isotherms) and determined values that had the same ratio as the DFT. We were also able to correct the constant H₂O pressure data by using the experimental H₂O coverage reaction order. We measured the E_{app} for H₂ adsorption using FTIR and found that it agreed with the H₂ oxidation values. Further DFT analysis showed that the charge from the hydride (adsorbed to Au) is efficiently transferred in to the support O's, whereas it resided on the Au when the additional H₂O layer was present. Bond length analysis revealed that the hydroxyl that accepts the proton elongates substantially more when there isn't H₂O. We speculate that the elongation of the hydroxyl is unfavorable due to the disturbance of the hydrogen-bonding network. This is a new interpretation for the inhibiting effects of H₂O; the physisorbed molecules appear to decrease the TiO₂ reducibility. This surprising discovery has implications in general catalytic systems by offering an explanation for why H₂O inhibits certain reactions, and in turn revealing more about the reactions mechanism, allowing for opportunities to optimize catalysts.

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35. Effects of Alkaline Earth Cations in the Rational Design and Synthesis of Zeolites

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Zeolites are microporous aluminosilicates that have been widely used as commercial heterogeneous catalysts, adsorbents, and ion-exchange materials due to their unique porosity, acidity and hydrothermal stability. There are currently over 230 known zeolite framework types, and the vast majority of these structures are prepared synthetically under hydrothermal conditions in alkaline media, involving the use of organic structure-directing agents (OSDAs) that mediate the assembly of channels and cages within the porous network of zeolite crystals.¹ Due to the economic and environmental disadvantages of these organics, it is desirable to synthesize zeolites in the absence of organics, but reportedly less than 15 % of zeolite structures have been made in OSDA-free syntheses.² Here, we present a study of parameters that influence zeolite crystallization by developing ternary kinetic phase diagrams with respect to the molar composition of primary synthesis components. Moreover, we systematically introduce multivalent ions (e.g. alkaline earth cations) in syntheses, aiming to explore facile and cost-efficient methods to obtain crystal structures without the aid of OSDAs. Our findings reveal that the encapsulation of alkaline earth cations has a remarkable impact on the kinetics of zeolite crystallization (i.e. dramatically reduced times of synthesis) and can effectively tune the formation of zeolite frameworks under mild synthetic conditions (e.g. reduced temperatures). Here, we will present the results of this work, including the introduction of ternary (kinetic) phase diagrams that quantitatively illustrate pure-phase and multi-phase regions of zeolite structures.

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36. Enhanced CO and C₃H₆ Conversions on Spinel Catalysts: Impact of Catalyst Architecture

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Three-way catalysts (TWC) are used in gasoline vehicles to simultaneously eliminate CO, NO_x and hydrocarbons. Ceria has been widely utilized in TWC as the oxygen storage material (OSM) for enhanced oxidation (of CO, H₂, HC) and reduction (of NO and NO₂) since its introduction by Ford [1]. Recently researchers [2] reported that spinel-type mixed metal oxides exhibit excellent oxygen storage capacity (OSC) and can reduce precious group metal (PGM) loading requirements. We studied in a bench scale reactor the abatement of CO and C₃H₆ over a series of (PGM)-OSM catalysts with near-stoichiometric feed under steady-state and lean-rich modulation conditions. Mn_{0.5}Fe_{2.5}O₄ was used as the model spinel and conventional zirconia stabilized ceria (CZO) was used as a reference. The results show that the addition of spinel leads to the enhanced CO and C₃H₆ conversion, especially for C₃H₆. The dual-layer design (top PGM layer and bottom spinel layer) results in the best performance while the single layer design with direct deposited PGM onto OSM is the best for CZO. The study provides insight into the beneficial impact of oxygen storage material and provides guidance for optimization of TWC catalyst formulation.

Monolith samples were provided by CDTi Advanced Materials Inc., including PGM-only, OSM-only and PGM-OSM catalysts. The studied OSMs include spinel (Mn_{0.5}Fe_{2.5}O₄) and CZO. Two monolith different architecture PGM-OSM monolith samples were used: the first is a single layer with PGM dispersed on OSM; the second is a dual-layer with a top PGM layer and a bottom OSM layer. For brevity, the PGM-only sample was denoted as “PA” and the spinel-only sample was denoted as “SA”. The PGM-spinel samples with single or dual layer design were denoted as “PSS” or “PSD” respectively. All catalysts were pre-aged in static air at 700 °C for 33 hrs before testing.

A series simple stoichiometric feed was used to study the light-off behavior of CO and C₃H₆. Also, another complex stoichiometric feed was used to mimic the realistic exhaust conditions. The complex feed had the composition of 500 ppm NO, 0.17% H₂, 0.52% CO, 400 ppm C₃H₆, 0.5% O₂, 7% CO₂, 7% H₂O. Both feeds had a space velocity of 70 k hr⁻¹. A FTIR (Thermo Scientific, Nicolet 6700) measured the effluent concentrations in the bench reactor system.

Figure 1 shows the C₃H₆ light-off curve over either PGM-only (PA) or spinel-only (SA) catalysts in a simple stoichiometric feed with a ramp rate as 10 °C/min. Both SA and PA result in similar T₅₀ value (temperature giving 50% conversion) at ~ 400 °C. In comparison with SA, a ~ 40 °C lower T₈₀ value (temperature giving 80% conversion) is achieved for PA. Although not shown here, the oxidation of C₃H₆ over spinel is unaffected by the presence of CO while the oxidation of C₃H₆ over PA is inhibited by CO.

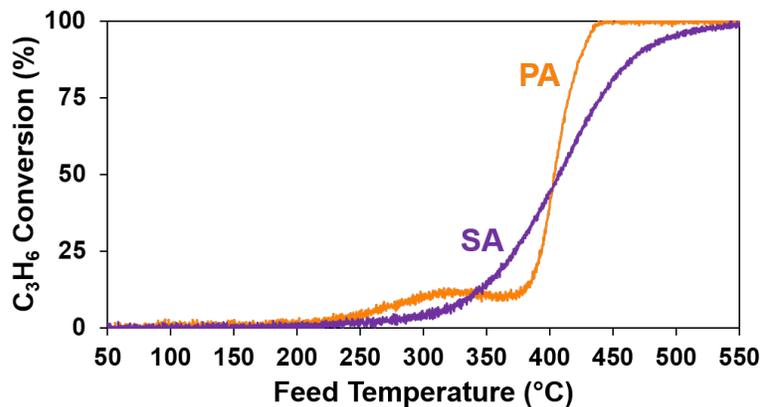


Figure 1. Propylene conversion as a function of feed temperature on spinel-only and PGM-only catalysts [Conditions: ramp rate: 10 C/min; feed: 400ppm C₃H₆, 0.18% O₂, balance Ar].

Figure 2 shows the cycle-averaged CO and C₃H₆ conversion over PGM-only (PA) and PGM-spinel (PSD and PSS) samples using the stoichiometric steady feed from 200°C to 500°C. The results obtained on PA is used as a reference. The addition of spinel (PSD and PSS) promotes CO and C₃H₆ light-off, confirming the promotional impact from spinel. In comparison to PA, a ~ 50 °C lower T₅₀ value is achieved for both CO and C₃H₆ conversion with the single-layer design (PSS). The promotional impact from spinel is more exaggerated with the dual-layer design, resulting in a ~ 70 °C lower T₅₀ value for both CO and C₃H₆ conversion. Although not shown here, CO conversion is enhanced by addition of spinel and the dual layer design (PSD) provides the largest promotional impacts.

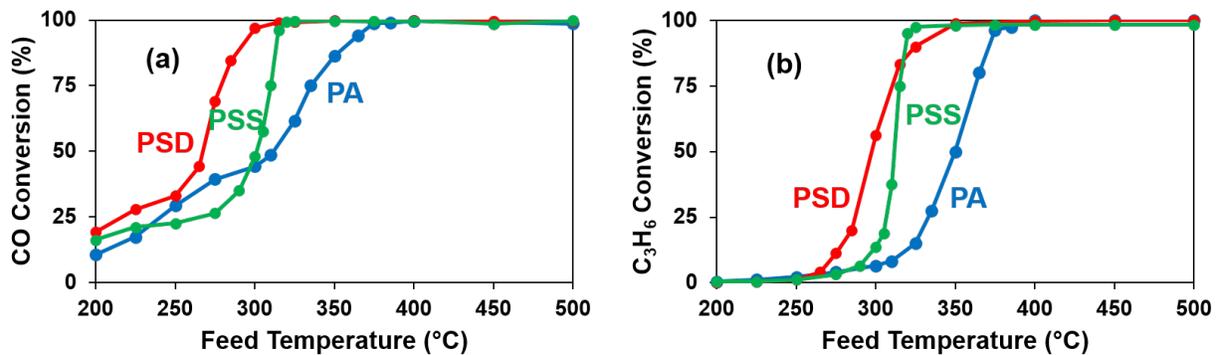


Figure 2. Cycle-averaged CO and C₃H₆ conversion as a function of feed temperature on spinel contained samples with PGM-only sample as reference. [Conditions: steady-state feed: 500ppm NO, 0.17% H₂, 0.52% CO, 400 ppm C₃H₆, 7% CO₂, 7% H₂O, balance Ar].

The reactor data will be supplemented with measurements of the cumulative and dynamic oxygen storage capacity of the materials. The collective results will be interpreted with a phenomenological mechanism.

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A Brief History of the Southwest Catalysis Society

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

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

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

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

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

In addition, catalysis groups were springing up at several universities, including surface science by the late John Mike White at the University of Texas, Jack Lunsford's and Wayne Goodman's highly productive groups at Texas A&M, Richard Gonzales at Tulane, Jim Richardson at U of H, Kerry Dooley



at LSU, Tom Leland and me at Rice, and groups at other universities in the 5-state area. What was lacking? There was no formal mechanism for these diverse groups to exchange information or get advice in the southwest. The time was ripe for an organization where catalysis could be openly discussed. Although much catalysis research is proprietary, enough was sufficiently open to create a stimulating environment for sharing mutual interests, many focusing on new ultra-high vacuum analytical equipment that was being rapidly developed.

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

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

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