

SOUTHWEST CATALYSIS SOCIETY

2015 SPRING SYMPOSIUM

Friday, April 24, 2015

Melcher Hall, Room 160

University of Houston, Houston, TX

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The SWCS officers and I welcome you to the 2015 SWCS Spring Symposium, **Friday, April 24, 2015**, at the University of Houston in Melcher Hall, Room 160 (building #528 on the University of Houston map on the back page).

We are delighted to present six invited speakers and 27 poster presentations for this year's meeting. Meritorious posters presented by students and post-docs will be identified with **Best Poster Awards**, carrying cash prizes. The poster session will be held in the hallway of Melcher Hall just outside Room 160.

The 2015 Spring Symposium **registration fee is \$50**, which includes North American Catalysis Society and SWCS annual membership dues, along with coffee/snack breaks. To speed registration, provide your business card along with your registration fee. You can also pre-register on-line through our pay-pal account

We will be able to accept credit cards (Visa, MasterCard, Discover, and American Express) for the registration fee or corporate donations. Credit card receipts will be sent via e-mail, so please be prepared to input your e-mail address into our system when you pay. But note, that checks are faster (especially if you have them ready to go). We will also continue to accept cash.

If you have colleagues who cannot attend the Symposium, please forward this program to them and let know they can mail their membership dues (\$50) to our Treasurer, Victor Johnston (mailing address shown at left).

Checks should be made out to SWCS.

The student registration fee is \$10, which includes NACS and SWCS membership.

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

We hope you enjoy the symposium!

Dan Shantz
Tulane University
Chair

2015 PROGRAM

All talks & breaks will be held in Melcher Hall, Room 160

- 7:30 AM** Registration – Victor Johnston, Treasurer (& helpers)
- 8:25 AM** Welcoming Remarks – Dan Shantz, Chair
- 8:30 AM** Bob Weber, Pacific Northwest National Lab “Heterogeneous Catalysis in Complex, Condensed Reaction Media”
- 9:15 AM** Suljo Linic, University of Michigan, “Electrochemical Oxygen Reduction: Kinetic analysis and the development of Ag- and Pt-alloy catalysts for low temperature fuel cells”
- 10:00 AM** Coffee Break
- 10:30 AM** William Schneider, Notre Dame, “NO_x Catalysis from the Bottom Up”
- 11:15 AM** Jinguang Chen, Columbia University, “Design of Catalysts and Electrocatalysts for Energy Applications”
- 12:00 PM** Lunch Break and poster session (hallway outside Room 160)
- 1:30 PM** **Southwest Catalysis Society Excellence in Applied Catalysis Award**
Mike Wong, Rice University
- 1:45 PM** Mark Bussell, Western Washington University, “Nanoscale nickel phosphide catalysts for hydrodenitrogenation and hydrodesulfurization: In situ preparation at low temperature”
- 2:30 PM** Ye Xu, Louisiana State University, “Role of Oxygen Vacancy in the Surface Reactivity of CeO₂(111)”
- 3:15 PM** Poster Awards and SWCS Business Meeting
In Melcher Hall, Room 160
- 3:30 PM** Adjourn

Heterogeneous Catalysis in Complex, Condensed Reaction Media

Robert S. Weber

Pacific Northwest National Laboratory, Institute for Integrated Catalysis



Many of the reactions required to upgrade biomass into fuels and chemicals—hydrogenation, hydrodeoxygenation, hydrocracking—are ostensibly similar to those practiced in the upgrading of petroleum into fuels. But, repurposing hydroprocessing catalysts from refinery operations has proved to be unsatisfactory. New *catalysts* are needed because the composition of the biogenic reactants differs from that of petroleum-derived feedstocks (e.g. the low concentration of sulfur in cellulose-derived biomass precludes use of metal sulfide catalysts unless sulfur is added to the reaction stream). New *processes* are needed because bio-oils oligomerize rapidly, forming intractable coke and “gunk”, at temperatures so low that the desired upgrading reactions are impractically slow, and so low that the bio-oil upgrading must be handled as a condensed fluid. Ideally, the new catalysts and processes would exploit the properties of the multiple phases present in condensed bio-oil, notably the polarizability and structure of the fluid near a catalyst’s surface.

This presentation will introduce a new type of support effect, for which there is evidence from homogeneous catalysis, and will discuss ways to implement and measure the hypothesized support effect and steer surface-catalyzed reactions to promote novel reaction mechanisms and to decrease catalyst deactivation.

Electrochemical Oxygen Reduction: Kinetic Analysis and the Development of Ag- and Pt-alloy Catalysts for Low Temperature Fuel Cells

Suljo Linic (ACS Catalysis Lecture)

Professor and 1938 Faculty Scholar
Director, Energy Systems Engineering Program
Department of Chemical Engineering
University of Michigan



The oxygen reduction reaction (ORR) is the major source of overpotential loss in low-temperature fuel cells. Expensive, Pt-based materials have been found to be the most effective catalysts, but exploration of alternatives has been hampered by stability constraints at the typical operating conditions of low pH and high potential.

I will discuss our studies of elementary mechanism of ORR on various metal electrodes using kinetic and micro-kinetic analysis of reaction pathways and quantum chemical calculations. These studies allowed us to identify the elementary steps and molecular descriptors that govern the rate of ORR. Using these performance descriptors we have been able to identify families of Pt and Ag-based alloys that exhibit superior ORR performance in acid and base respectively.

We have synthesized these alloys to demonstrate the superior ORR activity with rotating disk electrode experiments. We have also performed thorough structural characterization of the bulk and surface properties with a combination of cyclic voltammetry, x-ray diffraction, and electron microscopy with spatially resolved energy-dispersive x-ray spectroscopy and electron energy loss spectroscopy.

NO_x Catalysis from the Bottom Up

William F. Schneider

Professor of Chemical and Biomolecular Engineering
Notre Dame University



In order to meet the increasing demands of energy sustainability and environmental protection, catalysis science and application in the 21st century has to be driven by basic insights into how catalytic materials function and how they can be improved. The advent of first-principles simulations based on density functional theory (DFT), which are able to reliably simulate chemical structures and reactions at the molecular scale, has been instrumental in the recent renaissance in heterogeneous catalysis research. In this talk, I will illustrate the capabilities and challenges of applying these simulation tools in the context of the catalytic chemistry of nitrogen oxides (NO_x). NO_x is an unwanted by-product of combustion and is particularly difficult to remove from lean combustion sources, such as diesel engines. NO_x also has rather complex chemistry that presents special challenges to simulation. I will describe some of our successes in understanding NO_x chemistry from first-principles, with a first emphasis on recent work to capture the essential features of the beguilingly simple catalytic oxidation of NO to NO₂ over metals and metal oxides, to reconcile these models with experimental results, and to use these insights to guide the selection of new and improved catalysts. I will then discuss recent work to extend the same concepts to the selective catalytic reduction of NO_x over narrow-pore metal-exchanged zeolites, a new class of effective and stable catalysts.

Design of Catalysts and Electrocatalysts for Energy Applications

Jingguang G. Chen (ACS Olah Award winner)

Thayer Lindsley Professor of Chemical Engineering
Columbia University



In the current talk we will use two examples to demonstrate the importance of using fundamental studies to identify and design catalysts and electrocatalysts. Our research approaches involve parallel efforts in density functional theory (DFT) calculations, surface science experiments on model systems, and synthesis and evaluation of supported catalysts under thermochemical or electrochemical conditions. We will first use water electrolysis to demonstrate the feasibility of using one atomic layer (monolayer) Pt on transition metal carbides (TMC) to achieve the same activity as bulk Pt. We will present DFT calculations of similar electronic and chemical properties between monolayer Pt/TMC and Pt, synthesis and characterization of monolayer Pt/TMC films, and electrochemical evaluation of the activity and stability of Pt/TMC for water electrolysis. Compared to the state-of-the-art Pt electrocatalyst, monolayer Pt/TMC catalysts represent a significant reduction in Pt loading for water electrolysis.

We will then use the conversion of biomass-derived oxygenates as an example to illustrate the advantages of bimetallic catalysts, which often show unique activity and selectivity over the corresponding parent metals due to the electronic modification and strain effect. We will present our results on the characterization of Ni/Pt bimetallic model surfaces and supported catalysts under in-situ reaction conditions, further highlighting the importance of using the combined approaches of DFT calculations, surface science experiments, and reactor evaluation for catalyst discovery.

Southwest Catalysis Society Excellence in Applied Catalysis Award
Professor Michael Wong, Rice University

Nanoscale Nickel Phosphide Catalysts for Hydrodenitrogenation and Hydrodesulfurization: In situ Preparation at Low Temperature

Mark E. Bussell

Professor

Department of Chemistry and Advanced Materials Science and Engineering Center
Western Washington University



Transition metal phosphides show excellent promise for hydrotreating reactions and the most active phosphides (e.g. Ni₂P/SiO₂) have exhibited higher hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activities than commercial sulfided Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts. However, the conventional synthesis of metal phosphide catalysts, which involves temperature-programmed reduction (TPR) of phosphate-based precursors, requires temperatures as high as 1100 K to produce the active phase. In addition, the strong interaction of phosphate with Al-containing supports complicates reduction of metal phosphate precursors on alumina (Al₂O₃), amorphous silica-alumina (ASA, SiO₂-Al₂O₃) and zeolites, and often results in poor performing catalysts relative to silica-supported metal phosphides. High reduction temperatures and the lack of versatility for supports make the use of metal phosphide catalysts less desirable for industrial hydrotreating applications. In this study, a novel synthesis method is described for the preparation of Ni₂P on SiO₂, Al₂O₃ and ASA from nickel hypophosphite precursors at 573-673 K. The results of a detailed investigation of the synthesis using TPR with on-line mass spectrometry (TPR-MS) will be presented. The in situ prepared Ni₂P catalysts exhibit high activities for the HDN of carbazole and HDS of benzothiophene, with the Ni₂P/Al₂O₃ and Ni₂P/ASA catalysts over three and two times more active, respectively, than similar catalysts prepared from nickel phosphate precursors.

Role of Oxygen Vacancy in the Surface Reactivity of CeO₂(111)

Ye Xu

Assistant Professor of Chemical Engineering
Louisiana State University



Ceria is an abundant and widely used technological material owing to its ability to readily store and release oxygen and change oxidation state. There is a growing body of studies indicating that ceria exhibits significantly different catalytic reactivity, including redox and C-C coupling reactions, toward a given organic molecule depending on the extent of reduction and crystalline orientation of the surface. This suggests that ceria is a promising candidate for the development of heterogeneous catalysts for the conversion of organic compounds, if its reactivity can be understood and tailored at the atomic level. In this talk I will discuss the roles of oxygen vacancy in the activation of simple organic oxygenates including acetaldehyde, formic acid, and acetic acid on the CeO₂(111) surface. Proposed reaction pathways and surface reaction intermediates are explored and calculated using density functional theory, followed by microkinetic modeling and simulation of infrared spectra. The results are compared with available surface science experiments performed under controlled conditions, to elucidate the fundamental mechanisms through which these molecules interact with CeO₂(111).

POSTER ABSTRACTS

1. Improved CO₂ Capture Technology with Low Temperature Catalytic Desorption

Mayank Gupta¹, Zhen Wang, Colin Shaw and Michael S. Wong^{1, 2, 3*}

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Chemical absorption of CO₂ by an aqueous amine is one of the most effective techniques for post-combustion CO₂ capture. However, commercial applications are restricted due to high energy cost associated with this technology. More than 50% energy penalty incur from regeneration of the solvent at high temperatures. We have developed a novel process which can potentially reduce the cost of existing amine-based CO₂ capture technology by lowering temperature and thus the energy requirement. In addition to this, problems such as degradation and evaporation of amines will be significantly reduced or eliminated. Our process involves enhanced desorption of CO₂ from a spent monoethanolamine (MEA) solution at lower temperatures than conventional methods. Low desorption temperature was achieved by adding a catalyst to the MEA solution during its regeneration.

2. Grain Structures and Boundaries on Microcrystalline Copper Covered with an Octadecanethiol Monolayer Revealed by Sum Frequency Generation Microscopy

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An octadecanethiol (ODT) self-assembled monolayer on microcrystalline copper was investigated by sum frequency generation (SFG) imaging microscopy. The crystal grain and grain boundaries of the copper surface were mapped in the SFG image based on the strong brightness contrast of the SFG signal across the boundary. Local SFG spectra reveal significant difference with each other, as well as the average SFG spectra, indicating the heterogeneity of the copper surface resulting from copper grains with distinct crystallographic facets and orientations. It is demonstrated that the SFG signal of crystalline domain areas contains azimuthal anisotropy with respect to the plane of incidence. In addition, the statistical orientation analyses of amplitude ratio of CH₃-sym/CH₃-asym and corresponding contour maps imply that the orientation of ODT molecules is affected by the underlying copper.

3. Importance of the Material Gap for the Rational Design of Pd Catalysts for Complete Methane Oxidation

Hieu A. Doan, Munish K. Sharma, William S. Epling and Lars C. Grabow*

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Recent technological advancements in horizontal drilling and hydraulic fracturing have enabled the extraction of shale gas and made natural gas a very promising alternative to coal and petroleum-based fuels for energy production and transportation, respectively.¹ However, methane, which is the main constituent of natural gas, can cause detrimental greenhouse effects if it is not completely consumed in the combustion chamber.² The difficulty in methane combustion arises from the molecules' stable geometry, and therefore the first C-H bond breaking, or methane activation, is often considered the rate-limiting step.³ In this study, we employed Density Functional Theory (DFT) to screen for promising promoters that lower the energy barrier required for methane

activation on relevant surface models of Pd catalysts, such as Pd(100), Pd(211), PdO(101), and Pd/ γ -Al₂O₃. Our DFT calculations consistently identified Pt, Ni and Cu as potential dopants for Pd catalysts regardless of the surface model used. Temperature programmed oxidation experiments were carried out for the computationally predicted promoted catalyst candidates and the results showed an identical trend in catalytic activity as the theoretical predictions. Although the quantitative results vary between surface models, our study suggests that catalytic trend predictions are less sensitive to the choice of active site model and the resulting material gap.

- (1) Simakov, D. S. A.; Wright, M. M.; Ahmed, S.; Mokheimer, E. M. A.; Román-Leshkov, Y. *Catal. Sci. Technol.* 2015, **5**, 1991–2016.
- (2) Choudhary, T. .; Banerjee, S.; Choudhary, V.; *Appl. Catal. A Gen.* 2002, **234**, 1–23.
- (3) Trincherro, A.; Hellman, A.; Grönbeck, H.; *Surf. Sci.* 2013, **616**, 206–213.

4. SO₂ storage and release over γ -Al₂O₃ and Pt/ γ -Al₂O₃ catalysts: A combined experimental and kinetic study

Tayebeh Hamzehlouyan, Chaitanya Sampara and William Epling*

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In order to understand the transient phenomena that occur upon a diesel oxidation catalyst's (DOC) exposure to SO₂, SO₂ storage and release on/from γ -Al₂O₃ and Pt/ γ -Al₂O₃ were studied. Temperature programmed desorption (TPD) and *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were performed to understand the adsorption, surface reaction and desorption dynamics. The support effect was decoupled by using γ -Al₂O₃ samples in the experiments. Adsorption data verified that γ -Al₂O₃ as a catalyst support significantly affects the SO₂ storage and release of a Pt/ γ -Al₂O₃ catalyst. According to our experimental results, multiple sulfur species form during SO₂ adsorption on γ -Al₂O₃ and Pt/ γ -Al₂O₃. SO₂ adsorbed as molecular SO₂ on Al sites, as surface sulfites/bi-sulfites and surface sulfates on electron deficient oxygen sites as well as bulk aluminum sulfate were identified as adsorbed species on γ -Al₂O₃ and Pt/ γ -Al₂O₃. The results show that Pt has a promoting effect on surface sulfate formation as well as on spillover of surface sulfates into the bulk alumina support. A transient multi-step kinetic model was developed based on the experimental data to describe these effects in a single channel of the monolith. Based on the DRIFTS and TPD study, multi-step reaction mechanisms were proposed for SO₂ adsorption and desorption on γ -Al₂O₃ and Pt/ γ -Al₂O₃. The kinetic parameters were optimized to describe the TPD experimental data. The kinetic models were able to accurately predict the experimental behavior of the catalyst. Similar steady state coverage profiles along the monolith channel were predicted by the model irrespective of inlet concentrations for long exposure times, suggesting that low SO₂ concentrations typically seen in diesel exhaust can be simulated with higher concentrations to accelerate the sulfur effects.

5. Rational design of one-dimensional zeolites: Pathways to control crystal growth

Rui Li and Jeffrey D. Rimer

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Zeolites possess well-defined pores that provide desired shape selectivity for chemical reactions, which is one essential advantage of their commercial use as catalysts. The use of zeolites with one-dimensional (1D) pores can lead to more desirable selectivity in select processes, such as isomerization, cracking, and methanol-to-hydrocarbon (MTH) reactions. However, large diffusion limitations attributed to poorly engineered crystal size and habit often lead to rapid coking, which imposes restraints on the commercial viability of 1D zeolites. Here, we will present a systematic study of the synthesis and rational design of two industrially-relevant 1D zeolite catalysts, LTL and TON framework types. We have developed novel approaches in our group to enhance the catalytic performance of these materials through molecular design, employing zeolite growth modifiers

(ZGMs)¹ to tailor the size and habit of these 1D zeolite crystals. Moreover, we have investigated the pathways of zeolite crystallization, which predominantly occur via non-classical mechanisms involving the formation of so-called “worm-like particle” (WLP) precursors. To this end, we have studied the compositional and structural evolution of precursors and the effect of synthesis parameters on crystal morphology. We have also performed a rigorous screening of ZGMs for TON growth and identified molecules that are capable of effectively tuning the aspect ratio of TON crystals. Our study of 1D zeolite design reveals new possibilities for improving the physicochemical properties of these materials for various catalytic applications.²

(1) Lupulescu, A. I.; Kumar, M.; Rimer, J. D. *Journal of the American Chemical Society* 2013, **135**, 6608.

(2) Teketel, S.; Skistad, W.; Benard, S.; Olsbye, U.; Lillerud, K. P.; Beato, P.; Svelle, S. *ACS Catalysis* 2012, **2**, 26.

6. Activity Trends for CO and NO Co-Oxidation Catalysts at Low Temperature Diesel Emission Conditions

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Diesel engine emissions typically include CO, hydrocarbons (HC), NO_x and particulate matter (PM), all of which have an adverse effect on the environment. In order to reduce the environmental impact of diesel emissions, low temperature combustion (LTC) engines have been developed. LTC engines are more fuel-efficient and can effectively reduce the emission of NO_x and PM. However, at the intermediate to low temperature of LTC engine exhaust, the commonly used diesel oxidation catalyst (DOC) - Pt and Pd alloys are insufficient. New catalysts are needed to increase the DOC activity at low temperature.

In this work, we studied the NO oxidation reaction on two different sites of several late transition metals. The binding energy of each species and activation energies are calculated using density function theory (DFT) and obey a linear adsorption energy and transition state scaling relation. Combined with existing linear scaling relations for CO oxidation in the literature,¹ a two descriptor based micro-kinetic model can be built for the CO and NO co-oxidation reaction at different reaction conditions, from which we can obtain volcano plots showing catalytic activity trends. As expected, Pt and Pd are shown to have the highest oxidation activity at 600 K, while our results indicate that the volcano top moves closer to the Ag/Au region at 425 K. Our analysis suggests that alloys of Ag/Au and another precious metal may have better performance at moderate temperatures. From several alloys tested, Ag/Cu and Au/Cu alloys with a 3:1 ratio were found to have the best performance. Notably, if a Pt/Pd catalyst is used, any produced NO₂ will immediately react with CO to generate NO, which is undesired. Ag₃Cu or Au₃Cu alloys, on the other hand, do not efficiently catalyze the NO₂ + CO reaction. Overall, our computational predictions are that Ag₃Cu and Au₃Cu alloys achieve higher catalytic activity than Pt or Pd, and can also oxidize CO and NO simultaneously, which is beneficial for tuning the conditions for the downstream selective catalytic reduction (SCR) unit.

(1) Jiang, T.; Mowbray, D. J.; Dobrin, S.; Falsig, H.; Hvolbæk, B.; Bligaard, T.; Nørskov, J. K. *J. Phys. Chem. C* **2009**, *113*, 10548–10553.

7. Investigation of the Methanol-to-DME Reaction Mechanism on H-ZSM-5 using van der Waals Corrected Density Functional Theory

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Conversion of methanol to olefins or hydrocarbons over acidic catalysts, in particular H-ZSM-5 (a 3-D zeolite with MFI framework), is a feasible route for the production of commodity chemicals and liquid fuels, and has

been a popular subject of catalytic studies. Although the overall process is very complicated, the first step is accepted to be methanol dehydration to dimethyl ether (DME). The formation of DME from methanol may proceed through two competing pathways. The associative pathway is characterized by the coadsorption of two methanol molecules followed by simultaneous formation of water and DME, while the dissociative pathway is initiated by water elimination and surface methoxy formation from a single methanol molecule followed by DME formation after a second methanol molecule adsorbs.

The active sites of H-ZSM-5 are Brønsted acid sites that can be found in 12 distinguishable locations, which may be found in the sinusoidal or straight channels, or at the channel intersections. Here, we use density functional theory (DFT) calculations with periodic boundary conditions to investigate the dominant reaction mechanism at industrially relevant conditions for various active site locations. Through Gibbs free energy calculations we estimate the sensitivity of reaction mechanism to temperature and pressure at which the reaction is conducted. Our results indicate that depending on conditions the reaction may proceed along one of the two proposed pathways or even both as long as active sites are found at geometrically different locations. The use of a dispersion-corrected functional (vdW-DF) enables our computational approach to account for the pore confinement effects at different active site locations. To investigate the sensitivity to the strength and density of acid sites, we first tuned the active site acidity by using three different heteroatom substitutions, *i.e.* aluminum, gallium, and indium at each specific location in the MFI unit cell and calculated the transition state energies for each substitution. We look into the impact of acid site density by comparing kinetic parameters of the associative mechanism for several acid site pairs. Our studies have shown that the collaborative effect of two neighboring acid sites may result in considerable differences compared to the single site model. In summary, the result of our DFT simulations can illuminate the underlying factors influencing the mechanism of the methanol-to-DME reaction over H-ZSM-5 and provide valuable insight into the design of improved catalysts.

8. Hydrodeoxygenation of furan on oxygen vacancy sites of MoO₃(010): A DFT investigation.

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MoO₃ is a promising candidate with high reactivity and selectivity for bio-oil upgrade via catalytic hydrodeoxygenation (HDO).¹ Its sulfur counterpart, MoS₂, is used in the well-studied hydrodesulfurization process (HDS). Here, we attempt an atomic-level comparison between the two related chemistries based on a prominent density functional theory (DFT) study of thiophene HDS on MoS₂.²

Similar to HDS, HDO requires the initial creation of an oxygen-vacancy site where the feed molecule can adsorb. We assessed the thermodynamic stability of three distinct oxygen vacancy sites on the MoO₃(010) surface using a detailed ab-initio thermodynamic phase diagram under typical reaction conditions. In our analysis we predict an asymmetric oxygen vacancy with two subsurface hydrogen atoms as the most stable surface termination.

Next, we used this most stable MoO₃(010) facet to investigate the elementary reaction steps for furan HDO. The potential energy diagram based on the thermodynamic stability of reaction intermediates suggests that the reaction pathways for thiophene HDS and furan HDO are similar. Activation barriers for elementary reactions further indicate that furan HDO on MoO₃ is facile. However, the oxygen vacancy formation on MoO₃(010) is slow. We also investigated furan HDO on RuO₂, which is the oxide analogue of RuS₂, the most active HDS catalyst. Furan HDO on RuO₂ is facile but catalyst stability and cost might render it uneconomical. Unraveling the similarities and differences between the two processes (HDO and HDS) will ultimately let us design a novel HDO catalyst for the commercial use of biomass for the production of chemicals and fuels.

(1) Prasomsri, T.; Nimmanwudipong, T.; Román-Leshkov, Y. *Energy Environ. Sci.* 2013, **6**, 1732.

(2) Moses, P. G.; Hinnemann, B.; Topsøe, H.; Nørskov, J. K. *J. Catal.* 2007, **248**, 188–203.

9. First-principles investigation for hydrodeoxygenation of oxygenated aromatic compounds over Ru/TiO₂(110)

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Catalytic conversion of oxygenated aromatic compounds (OACs) into oxygen-free compounds, or bio-oil upgrading, suffers from both poor selectivity and low conversion because the direct deoxygenation (DDO) is harder to activate than decarbonylation (DCN) or hydrogenation (HYD). A promising catalyst with good activity and selectivity toward DDO products for OACs is Ru/TiO₂, according to recent studies.¹ However, the nature of the active site and roles of the Ru cluster and TiO₂ support remain by and large unknown.

Using density functional theory (DFT) we have explored the hydrodeoxygenation (HDO) pathways of phenol and *m*-cresol over supported Ru/TiO₂. The catalyst was modeled as Ru(0001) surface and a 10-atom Ru cluster supported on TiO₂(110). The comparison of the HYD vs. DDO pathways for phenol on Ru(0001) indicates that HYD is fast and kinetically preferred over DDO, suggesting that metallic Ru is unselective for direct C-O scission. For the Ru₁₀/TiO₂ interface our results suggest that the presence of Ru on TiO₂ facilitates hydrogen delivery to TiO₂(110) and facilitates oxygen vacancy formation at the Ru/TiO₂ interface. Phenol and *m*-cresol subsequently adsorb via their hydroxyl groups to the formed vacancy, and energy barriers for the following C-O scissions in phenol and *m*-cresol are 0.78 eV and 0.71 eV, respectively. The eliminated OH group heals the TiO₂ vacancy, and the aromatic rings of phenol and *m*-cresol remain on the Ru cluster. Metallic Ru has known hydrogenation activity and the formation of benzene and toluene is assumed to be quasi-equilibrated. Because of the strong interaction of the aromatic ring with the Ru cluster desorption of benzene and toluene is ca. 1.4 eV endothermic. Based on our theoretical analysis and in agreement with experimental observations, the role of Ru is to activate hydrogen, while C-O scission requires an oxygen vacancy site near the Ru/TiO₂ interface.

(1) Omotoso, T.; Boonyasuwat, S.; Crossley, S. P. *Green Chem.* **2014**, *16*, 645–652.

10. The Axial Reaction Profiles in Diesel Oxidation Catalysts under Simulated Low Temperature Combustion Exhaust

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The diesel engine is a very efficient internal combustion engine, with one downside; the high oxygen concentrations remaining in the exhaust lead to difficulty reducing nitrogen oxide(s) (NO_x) present to nitrogen. Here is where new engine innovations, such as low temperature combustion (LTC) methods like reactivity controlled combustion, come in to play. Optimizing for the fuel efficiency of the engine, the inefficiencies leading to large amounts of NO_x formation can be mitigated leading to substantially lower levels present in the exhaust. The tradeoff for these LTC engines is that while there are substantial decreases in NO_x emissions, there are higher emissions of carbon monoxide and hydrocarbons by nearly an order of magnitude at certain operating conditions. For this reason it is important to understand the oxidation reactions occurring over the length of the diesel oxidation catalyst (DOC) designed to oxidize these components. This study looks at the reaction profile spatially resolved over the length of a Pt-Pd/Al₂O₃ monolith catalyst under simulated LTC diesel exhaust conditions. The simulated exhaust gas contains CO, C₂H₄, C₂H₆, C₁₂H₂₆, and NO. The species concentrations were measured along the length of the catalyst, as a function of time and temperature during temperature programmed oxidation experiments. The results show that the different components oxidize at different axial positions along the catalyst. Understanding these axial concentration gradients in the catalyst during these reactions will assist us in designing better DOCs in the future to enhance the low temperature catalyst performance, helping these new LTC engines meet environmental standards.



11. Rare Earth / Transition Metal Oxides for Syngas Cleanup

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

The mixed oxide catalysts (numbers represent molar ratios) Re/Ce₃/Zr₅₄, Ce₃/La, and Mn/Ce₄ give high and stable C₃ conversions with a low water (~10%) feed characteristic of the effluent from an air-blown gasifier. The catalyst FeCe₃ shows good C₃ reforming activity with both low and higher (>25%) water feeds characteristic of steam gasifiers. In parallel with this effort, DFT modeling was used to study both C-H and C-C bond activation on doped Ce(111) surfaces. Also, selected as-calcined and used catalysts were characterized by X-ray diffraction (XRD), X-ray absorption near edge structure (XANES), X-ray absorption fine structure (XAFS), temperature-programmed oxidation (TPO), temperature-programmed reduction (TPR), Raman spectroscopy, and magnetic susceptibility measurements. The characterizations showed that the catalysts remained (mostly) as doped REOs, without extensive phase separation.

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12. Polyolefin oligomers as solvents and tools for Ru(II)-catalyzed metathesis reactions

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Olefin metathesis has become an important method for carbon-carbon double bond formation.¹ In the past decade, there have been many developments in metathesis catalysis. In the case of Ru(II) catalysts this has included improvements in reactivity, stability, and selectivity.² However, a common issue to all metathesis procedures is the removal of ruthenium at the end of the reaction.³ Our work has approached this question in several ways. First, we have shown that we can prepare Ru(II) complexes with NHC ligands that contain non-polar polyolefin phase anchors starting with commercially available polyethylene (PE_{Olig}) and polyisobutylene (PIB) oligomers. The resulting PE_{Olig}-supported Hoveyda-Grubbs catalysts can affect both ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) reactions with separation of products and catalyst residues in a hydrocarbon solid wax phase. In these cases, the quantitative insolubility of these catalysts and the products' solubility allowed the products to be separated at room temperature as solutions from the insoluble catalysts. We have also investigated the use of various PIB-bound species both as ligands and/or sequestrants to recover Ru(II) after a catalytic reactions in heptane. For example, PIB-supported isocyanides like low molecular weight isocyanides act as a sequestering agents for metathesis catalysts. They

can also serve as sequestering reagents for Ru(II) catalysts that do not have other polymeric ligands. In this latter case, the quenched ruthenium catalysts can be separated from the product using a biphasic liquid/liquid separation. While specific Ru(II) contamination levels vary depending on the exact process used, both ROMP and RCM reactions can be carried out with polyolefin solvents and ligands such that Ru contamination in the products is less than 0.1%.

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13. Rapid hydrocarbon pulsing on a dual-layer LNT-SCR catalyst for low-temperature NO_x reduction

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Current NO_x emission control systems, selective catalytic reduction (SCR) and NO_x storage and reduction (NSR), function well at temperatures above 250 °C but have unsatisfactory NO_x conversion at lower temperature encountered during cold start and low engine load operation. SCR relies on an on-board urea dosing system to supply NH₃ that can selectively reduce NO_x under lean conditions over Fe- and Cu-exchanged zeolite catalysts. SCR cannot function when the exhaust temperature is below the minimum urea dosing temperature of ca. 200 °C. NSR involves cyclic operation over a lean NO_x trap (LNT) catalyst, which stores NO_x under lean feed, followed by regeneration by a short rich feed purge containing a mix of CO, H₂ and hydrocarbons (HC). At low feed temperature NSR suffers from inefficient utilization of some reductants (CO, HCs) and undesired byproduct formation (N₂O, NH₃) during low-T regeneration.

To address the challenge of low-T lean NO_x reduction, we have developed a new system with higher low-T deNO_x efficiency which utilizes high-frequency hydrocarbon pulsing over a dual layer LNT-SCR monolithic catalyst under lean feed conditions. This application was inspired by Di-Air (“Diesel NO_x aftertreatment by Adsorbed Intermediate Reductants) system recently developed by Toyota, in which rapid short-cycle injection of hydrocarbons significantly increased the LNT NO_x conversion at temperatures exceeding 400 °C.¹ The Di-Air mechanism involves the formation of short-lived N-containing hydrocarbon intermediates, which can be potentially captured and utilized by the SCR component of the dual-layer catalyst for incremental NO_x conversion. This goal of this study is to determine if and how a high-frequency HC pulsing can increase the low-T NO_x conversion of dual-layer LNT-SCR catalysts over that of a conventional NSR operation. Both chemical and thermal effects on the working mechanism for the low-T enhancement were investigated by bench flow reactor and in situ DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) experiments. We also discuss how variations of the catalyst configuration, PGM loading and zoning may optimize this new deNO_x system.

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14. Methane Activation by Surface Oxygen Species on Au₃Pd(111)

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The use of methane, the main component of natural gas, as feedstock for chemical industry is very appealing owing to its abundance and low cost.¹ In spite of these favorable facts, the potential for the production of value-added products from methane has not been fully realized. The primary challenge for methane utilization is the molecule's strong C–H bond and symmetric geometry without obvious point of attack.² Consequently, the rate-determining step for nearly all methane conversion reactions is the first C–H bond breaking step, or methane activation.³ Au-Pd/TiO₂ nanoparticles have been shown as highly effective catalysts for selective oxidation of methane to methanol using hydrogen peroxide as oxidant.⁴ The most likely active oxidants for the reaction are surface-bound OOH* and OH* species, which are derived from the surface decomposition of hydrogen peroxide. Alternatively, surface-bound OOH* and OH* can be synthesized directly from the reaction of water with oxygen at the Au/TiO₂ interface.⁵ In the view of this, our ongoing work builds on the hypothesis that selective (partial) oxidation of methane to methanol could be achieved in the presence of water and molecular oxygen over Au-based heterogeneous catalysts. Using density functional theory (DFT) we have explored methane activation pathways with and without surface oxygen species on a Au₃Pd(111) model surface. Our DFT results for the methane activation energy barrier in the absence of oxygen species on Au₃Pd(111) surface is consistent with results on the Pd(111) surface, suggesting that Pd provides the active site in this case.⁶ Further, our study indicates that surface oxygen species, such as OOH* and OH*, can lower the energy requirements for methane activation, which is a necessary requirement for the selective conversion of methane.

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15. Tailoring the Physicochemical Properties of Zeolite Catalysts through Molecular Design

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There are growing opportunities for the use of zeolite catalysts in a wide range of applications that span petrochemicals to biomass and natural gas conversion. Despite their extensive use in commercial processes, an understanding of their growth mechanism(s) remains elusive. The rational design of zeolite catalysts calls for more versatile synthetic approaches capable of tailoring crystal properties, such as crystal size, morphology, and composition. The ability to selectively tune these physicochemical properties can improve catalyst on-stream lifetime, conversion, and shape selectivity. Here we will discuss how a facile and economical approach employing zeolite growth modifiers (ZGMs) can lead to more predictive control of zeolite crystallization towards the optimization of commercial catalysts.

We will discuss the design of industrially-relevant zeolite catalysts. Our focus on materials with 1-D pores that exhibit restricted mass transport (LTL and MOR) and small-pore aperture (CHA) presents an opportunity to explore the impact of crystal engineering on targeted catalyst performance (e.g., activity and lifetime). To this end, we will discuss our studies of zeolite crystallization in the presence of ZGMs, which are molecules that selectively bind to specific surfaces of zeolite crystals and mediate anisotropic growth rates.¹ We systematically examined a library of modifiers ranging in their structure and functional moieties to assess the physicochemical properties that regulate their efficacy and specificity as zeolite crystal growth modifiers. As we will demonstrate, the judicious selection of ZGMs can markedly alter zeolite crystal morphology from high aspect ratio (needle-like) crystals and micron-sized spheroidal crystals to thin discs and small spheres, respectively, with concomitant reduction in the internal diffusion pathlength and external surface area. Our studies reveal that ZGMs permit the control of zeolite crystal size spanning more than three orders of magnitude. This work also revealed that ZGM hydrophobicity and the spatial sequencing of binding moieties are effective molecular descriptors of its efficacy.² Electrostatic interactions play an important role, and can be used to target different crystallographic faces. Using LTL for a benchmark study, we established general guidelines for modifier screening based on the molecular topology of the terminating crystal surface. Similarly, we have synthesized nano-size MOR and CHA crystals, which is difficult to accomplish by conventional synthesis routes. Lastly, we will present time-elapsd studies of crystallization in order to elucidate the impact of modifiers on zeolite nucleation and growth. We investigated the structural and molecular transformation of amorphous phase to crystalline phase using colloidal techniques, and explored growth pathways through the use of *in situ* solvothermal atomic force microscopy (AFM), which was pioneered in our group.³ Collectively, our findings reveal fundamental aspects of growth mechanisms and provide a platform for exploring structure-performance relationships in zeolite catalysis.

This work seeks to establish a commercially viable approach to optimize zeolite catalyst performance and to provide a framework for rational design. Our synthesis scheme using ZGMs to optimize crystal properties such as habit and surface roughness is advantageous for the manufacturing of catalysts with improved and tailored properties. Given the fact that ZGMs are inexpensive and recoverable (post-synthesis), this practical approach to crystal engineering has the potential to enhance the design of a variety of zeolite framework types for a range of commercial applications.

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16. Catalysts for the Positional Isomerization of Long-Chain Olefins

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Internal, long chain olefins (>C₁₂) are used in the production of paper sizing agents and as deep-sea drilling fluids. We studied the double-bond (positional) isomerization of C₁₆-C₁₈ olefins. Solid acids, such as sulfonated poly(styrene-co-divinylbenzene) (PS-DVB's), perfluorinated ion exchange resins, and acidic zeolites were tested in packed bed reactors to determine catalyst lifetime and selectivity to internal olefins. The most promising catalysts had high selectivity to internal olefins and slow deactivation. For PS-DVB's, cooperativity was found between acid site density and catalytic activity. Oligomer side-products were quantified; rate of oligomerization increased with acid site density. We are currently studying the regeneration of Nafion/SiO₂ catalysts using various heat and solvent treatments. The most effective treatments combine polar and nonpolar solvents at elevated temperatures.



17. The Effect of Pd Particle Size for Partial Oxidation of Methane on Al₂O₃ and TiO₂ Supports

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Partial oxidation of methane (POM) is an attractive alternative to methane steam reforming due to it being mildly exothermic and producing syngas to use as reactants in Fischer-Tropsch and methanol synthesis reactions.^{1,2} POM has been investigated extensively on noble metals such as Pd showing the reaction mechanism is dependent on the nature of the active sites.^{3,4} To gain further insight, the rate of methane consumption was related to the Pd particle size to determine if the reaction scales with the particle perimeter or area. Pd/Al₂O₃ shows rate of reaction increases on larger particles with no clear relationship between rate of reaction and particle size. The increase in reaction rate has been previously reported on Al₂O₃ and ZrO₂ and associated with the lack of oxygen vacancies on Pd caused by strong interactions between Pd and Al₂O₃.⁵ The rate of reaction for Pd supported on rutile TiO₂ declines with increasing particle size and scales with the perimeter as suspected.

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18. CO Oxidation on fresh and aged Pd/Al₂O₃ and Pd/Ceria-Zirconia/Al₂O₃ catalysts

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Three-way catalyst (TWC) light-off performance is critical in cost effectively meeting future emission standards. Improvements in catalyst light-off (LO) should include catalyst modifications that minimize inhibition effects of exhaust species, lowering precious group metal (PGM) loading, and using a lower cost PGM such as Pd. Zirconia-stabilized ceria on alumina provides high surface area and oxygen storage, and is known to enhance the oxidation of CO through mitigation of the CO inhibition.¹⁻³ In this work we study the LO behavior and isothermal, steady-state kinetics of CO oxidation under near-stoichiometric conditions using fresh and aged monolith catalysts synthesized with Pd and Al₂O₃ and/or ceria-zirconia (CZO) washcoat supports. Aging was carried out to mimic average aging catalysts experience over their full useful life. Light-off temperatures for CO oxidation on the aged Pd/CZO/Al₂O₃ catalyst are found to be notably higher than those on the fresh Pd/CZO/Al₂O₃ catalyst. Fresh Pd/CZO/Al₂O₃ and Pd/Al₂O₃ catalysts are found to have similar CO LO behavior. Kinetic parameters extracted from steady state experiments (reaction order and activation energies) are consistent with a CO desorption limited reaction on both Pd/CZO/Al₂O₃ and Pd/Al₂O₃ catalysts.

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19. Reaction Studies on $\text{Na}_2\text{WO}_4\text{-Mn/SiO}_2$ Catalyst for Oxidative Coupling of Methane

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

A large number of systems have been studied over the past few decades, but a catalyst and reactor concept has not been found that give sufficiently high C_{2+} yield. The most studied catalysts to date for the OCM reaction system have been alkali-promoted alkaline earth metal oxides, transition metal oxides and rare earth metal oxides. $\text{Na}_2\text{WO}_4\text{-Mn/SiO}_2$ catalyst has attracted a significant amount of attention because of its favorable catalytic performance. In this study we evaluate the activity of the catalyst in particulate and washcoat form using both fixed-bed and monolith reactor configurations.

The catalyst was prepared by the incipient wetness impregnation method and its structural properties were characterized by a variety of analytical techniques (e.g., XRD, BET, ICP and SEM). The prepared catalyst has a surface area of $2.6 \text{ m}^2/\text{g}$ and was sieved to a size of 50-70 mesh. Residence time variations were accomplished by changing the flow rate while keeping the weight constant.

We observed that, with higher CH_4/O_2 ratios and concentrated feed, the reactor system becomes quite sensitive to the operating conditions. In particular, the steep axial temperature limits the maximum oxygen concentration that can be used. By diluting the feed, the reaction can be conducted at higher CH_4/O_2 ratios. Washcoating is of particular interest since it reduces the contact time of C_2 hydrocarbons within the internal porous structure of the catalyst, thereby inhibiting deep oxidation.

20. Developing an Effective Methane Oxidation Catalyst for Cleanup of Natural Gas Vehicle Exhaust

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With the growing abundance of natural gas, its interest in use for vehicular applications is growing. One concern with natural gas engine vehicles is un-combusted methane exiting the engine and being exhausted to the environment. CH_4 is a known potent greenhouse gas, and thus limiting its emissions is of interest. A solution is a catalytic converter type of device, designed for natural gas engine exhaust. One significant challenge is the stability of the CH_4 molecule, typically requiring high catalyst temperatures to activate the CH_4 . In terms of active catalysts, previous studies have shown that Pd in its oxidized form is quite active. Palladium, however, can sinter under typical conditions, significantly reducing its activity over time. However, this activity drop can be retarded by either adding a promoter metal e.g. bimetallic platinum-palladium catalysts exhibit enhanced surface stability,¹⁻² or by adding oxides e.g. CeO_2 ,² or by changing support, i.e. using ZrO_2 instead of Al_2O_3 .³⁻⁵ The stability of these promoters against hydro-thermal aging is thus well established from prior research work.

In this study, experimental data were used to develop a CH_4 oxidation rate equation, which was in turn used in a single channel of the monolith model to simulate CH_4 oxidation. Additionally, the stability of the catalyst against hydrothermal aging was evaluated. Within the simulation environment, the hydrothermal aging effect was incorporated into the monolithic model.

The experimental data were obtained through temperature programmed oxidation (TPO) experiments, which were conducted under both dry and wet conditions using powder-based catalysts. Using the results, kinetic parameters were calculated. These results were then adjusted for an equivalent monolith-based amount of catalyst, calculated using the active site density. In the hydrothermal aging part of this experiment, different catalyst samples were aged at different temperatures. A predictive model was developed that captures the impact of hydrothermal aging. Catalyst aging reduces the number of exposed surface atoms which in turn decreases its active surface area and thus input data for the model is either the crystallite size or metal dispersion of the aged samples. This part of the model was incorporated in the overall monolith model by modifying the reaction rate constant. In this modified constant, the concentration of catalytic sites was separated from the rest of the temperature dependent factors. Except for a crystallite surface area that depends on its diameter, the rest of the quantities used in the model are either intrinsic or set by the experimental conditions.

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21. Tailoring ZSM-5 Crystal Morphology with Zeolite Growth Modifiers

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Zeolites are microporous, crystalline aluminosilicates with well-defined pore structures of molecular dimensions. With the combination of excellent shape-selectivity, strong Brønsted acidity and high hydrothermal stability, zeolites are often used as heterogeneous catalysts in refinery and petrochemical processes. ZSM-5 is one of the most commonly used zeolites in industrial processes. It has the framework of MFI, which has a 3-dimensional structure with straight channels oriented axially along the [010] direction. Molecule diffusion is much faster in these straight channels than in the sinusoidal channels, making the straight channels better suited for catalytic reactions. To this end, it is desirable to control the [010] thickness of ZSM-5 crystals.

In this work, we will use a novel approach to tailor ZSM-5 morphology that incorporates zeolite growth modifiers (ZGMs). The use of ZGMs has proven to be an efficient method to tailor the morphology of silicalite-1, which is a fully siliceous analogue of ZSM-5.¹ For our study of ZSM-5 synthesis in the presence of ZGMs, we first assessed the library of modifiers previously screened for silicalite-1. These studies assessed the effects of aluminum on ZGM efficacy. Here, we present this data along with an expanded ZGM library screening that includes organic molecules that have been shown to be effective for other zeolites (e.g. zeolite L).² With atomic force microscopy (AFM), we are using chemical force microscopy techniques to probe modifier-crystal interactions and examine the specificity of ZGM binding.

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22. Controlling Polymorphism in Organic-Free Syntheses of Zeolites

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The unique acidity, thermal stability, and shape-selectivity of nanoporous zeolites are utilized in industrial applications spanning catalysis to ion exchange. Difficulties in the formation of zeolites from organic-free growth media are prevalent, and the most common concern is the formation of undesirable crystal phase(s), i.e., impurities. Oftentimes, organic structure-directing agents (OSDAs) are used to form phase-pure crystals, though these additives are typically costly and must be removed by post-synthesis calcination. In order to both understand and control organic-free polymorphism, we constructed kinetic phase diagrams based on varying synthesis conditions using only inorganic ions (e.g., alkali metals) as the structure-directing agents.¹ These kinetic phase diagrams revealed regions of pure and mixed phases of eight zeolite framework types synthesized from colloidal silica and sodium aluminate.

Our systematic study has elucidated for the first time the phase behavior of GIS framework type, which exhibits two polymorphs: zeolites P1 and P2. By generating phase diagrams over a range of synthesis parameters, we have determined the conditions required to produce pure P1 and P2, and explored the kinetic pathways of each polymorph. Thermal stability tests have revealed increased stability from the P2 polymorph of GIS, providing the potential for application of this conventionally unstable structure at higher temperatures. Post-synthesis ion-exchange procedures to other cations (e.g., Na⁺ exchanged to Ca⁺²) resulted in a change in the structure to a third polymorph of the GIS framework that is the synthetic analogue to naturally occurring garronite.

We have extended these phase diagrams to examine less alkaline conditions and identified synthesis parameters that yield zeolite A (LTA framework), which is commonly reported with a silicon-to-aluminum ratio (SAR) of 1 without the use of any additives (e.g., OSDAs). By exploring unconventional synthesis conditions, we have been able to produce zeolite A crystals with a SAR of 2, which we call HOU-2, without the use of an OSDA.² Through this we have seen that utilizing ternary phase diagrams as a synthesis tool can provide guidance towards optimizing the physicochemical properties of zeolites while maintaining economically viable OSDA-free synthesis procedures.

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23. Formation of N-containing compounds: co-feeding NH₃ during FTS

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Fischer-Tropsch Synthesis (FTS) is a well known process for converting fossil sources like coal, via syngas (H₂ +CO), to synthetic fuel. In addition to fuel, a range of products with higher economic value are produced (e.g. olefins and oxygenates). Adding ammonia to the syngas feed during FTS results in the production of N-containing alkyl compounds.^{1,2} This includes marketable products such as aliphatic amines, nitriles & amides. One observation shared by previous authors was a decrease in oxygenate selectivity when the selectivity for the N-containing compounds increased.² In this work we aim to elucidate two important aspects of the reaction pathway, one pertaining to the initiation stage and the second to the termination stage. Ammonia is classically perceived as a poison in FTS. Thus, we would firstly like to know how the presence of NH₃, and its dehydrogenated counterparts – NH₂, NH & N, influence CO adsorption and dissociation. Density functional

theory (DFT) provides a valuable set of tools to investigate such fundamental reactions. We follow a methodology proposed by Ciobica et al.³ During FTS certain compounds, including oxygenates, undergo secondary reactions. Considering amination reactions and the observed changes in selectivity, we secondly want to know if the oxygenates are being consumed via a secondary reaction to afford the N-containing compounds. To test this assumption a series of co-feeding experiments were conducted in a slurry phase reactor ($T = 250\text{ }^{\circ}\text{C}$, $p = 5\text{ bar}$, $\text{H}_2/\text{CO} = 2:1$, $\text{GHSV} = 2250\text{ ml/g}_{\text{cat}}/\text{hr}$) and its products analyzed via comprehensive two-dimensional gas chromatography (GCxGC-FID/TOF). The information obtained from these techniques is used to expand our understanding of the reaction pathway for the N-containing compounds, and can ultimately aid in the design of a catalyst with the desired selectivity.

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

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Reductant effects of a fast lean-rich cycling strategy were investigated over a NO_x storage and reduction catalyst (NSR) containing Pt/Rh/BaO/CeO₂/Al₂O₃. As previous study shown, the cycle-averaged NO_x conversion increases with high frequency injection of propylene.¹⁻³ A systematically study was carried out to evaluate H₂, C₃H₆, C₃H₈ and hydrocarbon mixture reductants by both conventional NSR cycling and fast lean-rich cycling over a bench top reactor setup. Compared to C₃H₆ which is known to enhance NO_x reduction at fast injection frequency operation, the NO_x conversion is higher at conventional NSR cycling when using C₃H₈ as reductant at 250~325°C. Such phenomenon was attributed to the reaction order of different reductants respect to this NSR catalyst. Thus, several HC mixture were investigated to optimize the NO_x reduction performance for the fast lean-rich cycling strategy. With 12.5% C₃H₆ in the HC mixture, NO_x and C₃H₈ conversion were significantly increased below 300°C. At high temperature ($T > 325^{\circ}\text{C}$), the fast lean-rich cycling strategy enhanced NO_x reduction performance.

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

25. Rational Design of Zeolites for Methanol to Hydrocarbon Catalysis

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Sustainable development requires alternative sources of liquid hydrocarbon fuels and olefins. Methanol to hydrocarbons (MTH) is a key technology to bridge petrochemicals and non-oil carbon sources such as biomass, coal, and natural gas. The majority of catalysts used for MTH processes are zeolites; however, only H-ZSM-5 and H-SAPO-34 have been used in industrial MTH processes. A major focus of our research effort is to development new synthetic routes to optimize the performance of zeolite catalysts – most notably their on-stream lifetime (i.e., reduced coking).

The goal of our study is to synthesize high-performance, low-cost MTH catalysts by rational design. Initial studies have focused on ZSM-11, which reportedly has better lifetime than ZSM-5 in MTH.¹ Here we employ zeolite growth modifiers (ZGMs), which are site-specific molecules that are used to modulate anisotropic growth of zeolite crystals.^{2,3} In this study, ZGMs were used to reduce the size of ZSM-11 crystals in the (100)

and (010) dimensions, which results in a concomitant reduction in the internal diffusion path length of pores to improve catalyst lifetime. Here we will present the synergistic effects of optimizing both synthesis parameters and ZGMs to tailor the size and morphology of ZSM-11 crystals.⁴

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26. DFT Computational Studies of a Dirhodium Hydroformylation Catalyst

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In situ FT-IR and NMR spectroscopic data point to different $[\text{Rh}_2\text{H}_x(\mu\text{-CO})_y(\text{CO})_z(\text{rac-P4})]^{n+}$ hydroformylation catalysts in acetone and 30% water/acetone solvents. Gaussian DFT calculations have been extremely useful in providing support for the structures and mechanisms of these bimetallic catalysts. In acetone the primary catalyst species that reacts with alkene is the dicationic complex $[\text{Rh}_2\text{H}_2(\mu\text{-CO})_2(\text{CO})_2(\text{rac-P4})]^{2+}$. This fits our initial proposals and all the catalyst intermediates in the proposed catalytic cycle have been calculated along with many of the transition state energies. When water is added deprotonation of the dicationic hydride complex occurs to generate a monocationic mono-hydride catalyst species: $[\text{Rh}_2(\mu\text{-H})(\text{CO})_3(\text{rac-P4})]^+$. The DFT calculations clearly indicate that the active catalyst species usually only have a single bridging hydride or carbonyl, unlike the double-bridged dicationic catalysts. The proposed bimetallic monocationic mechanism has been fully computed and an updated mechanism will be presented.



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

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Reductant effects of a fast lean-rich cycling strategy were investigated over a NO_x storage and reduction catalyst (NSR) containing Pt/Rh/BaO/CeO₂/Al₂O₃. As previous studies showed, the cycle-averaged NO_x conversion increases with frequency injection of propylene resulting in an expansion in the temperature range giving high NO_x conversion [1-3]. A systematic study was carried out to compare the effectiveness of individual reductants H₂, C₃H₆, C₃H₈ and their mixtures during both conventional NSR cycling (~ 1 min cycle time) and fast lean-rich cycling (~10 s cycle time) in a bench-scale reactor system. In contrast to C₃H₆, which is known to enhance NO_x conversion during fast injection operation, C₃H₈ is less effective during higher frequency cycling in the feed temperature range 250~325°C.

The performance difference between the propene and propane is associated with the difference in their relative reactivities with oxygen; i.e. propene has a much lower light-off temperature than propane. Thus, several HC mixture were investigated to optimize the NO_x reduction performance for the fast lean-rich cycling strategy. For example, a reductant mixture containing 1:8 propene:propane resulted in significant NO_x conversion increases below 300°C. At high temperature (T > 325°C), the fast lean-rich cycling strategy enhanced NO_x reduction performance.

References

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- (2) Perng, C.C.Y.; Easterling, V.G.; Harold, M.P.; *Catal. Today* 2014, **231**, 125-134.
- (3) Zheng, Y.; Li, M.; Harold, M.; Luss, D.; *SAE Tech. Pap.* 2015, 2015-01-0984.



A Brief History of the Southwest Catalysis Society

As recounted by **Joe W. Hightower**, Professor Emeritus, Rice University (April 2009)
B.S. '59 - Harding University; M.S. '61 and Ph.D. '63 - The Johns Hopkins University

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

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

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

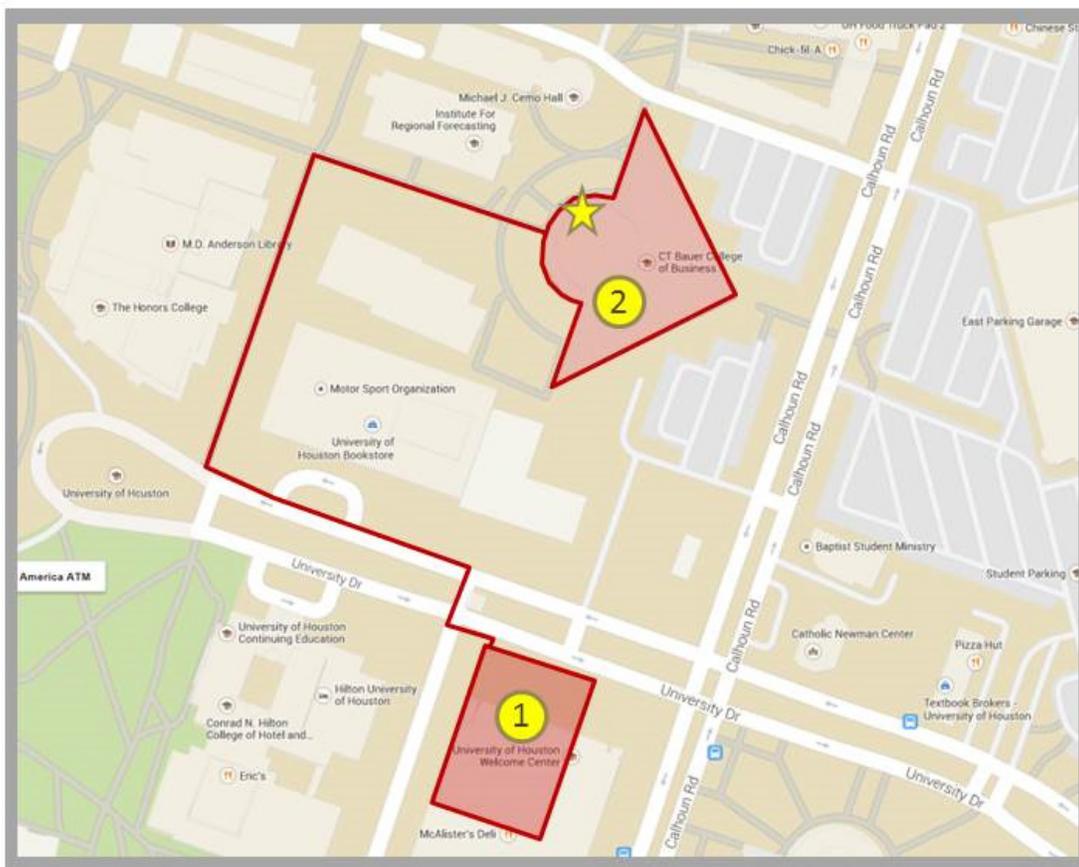
In addition, catalysis groups were springing up at several universities, including surface science by the late John Mike White at the University of Texas, Jack Lunsford's and Wayne Goodman's highly productive groups at Texas A&M, Richard Gonzales at Tulane, Jim Richardson at U of H, Kerry Dooley at LSU, Tom Leland and me at Rice, and groups at other universities in the 5-state area. What was lacking? There was no formal mechanism for these diverse groups to exchange information or get advice in the southwest. The time was ripe for an organization where catalysis could be openly discussed. Although much catalysis research is proprietary, enough was sufficiently open to create a stimulating environment for sharing mutual interests, many focusing on new ultra-high vacuum analytical equipment that was being rapidly developed.



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

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

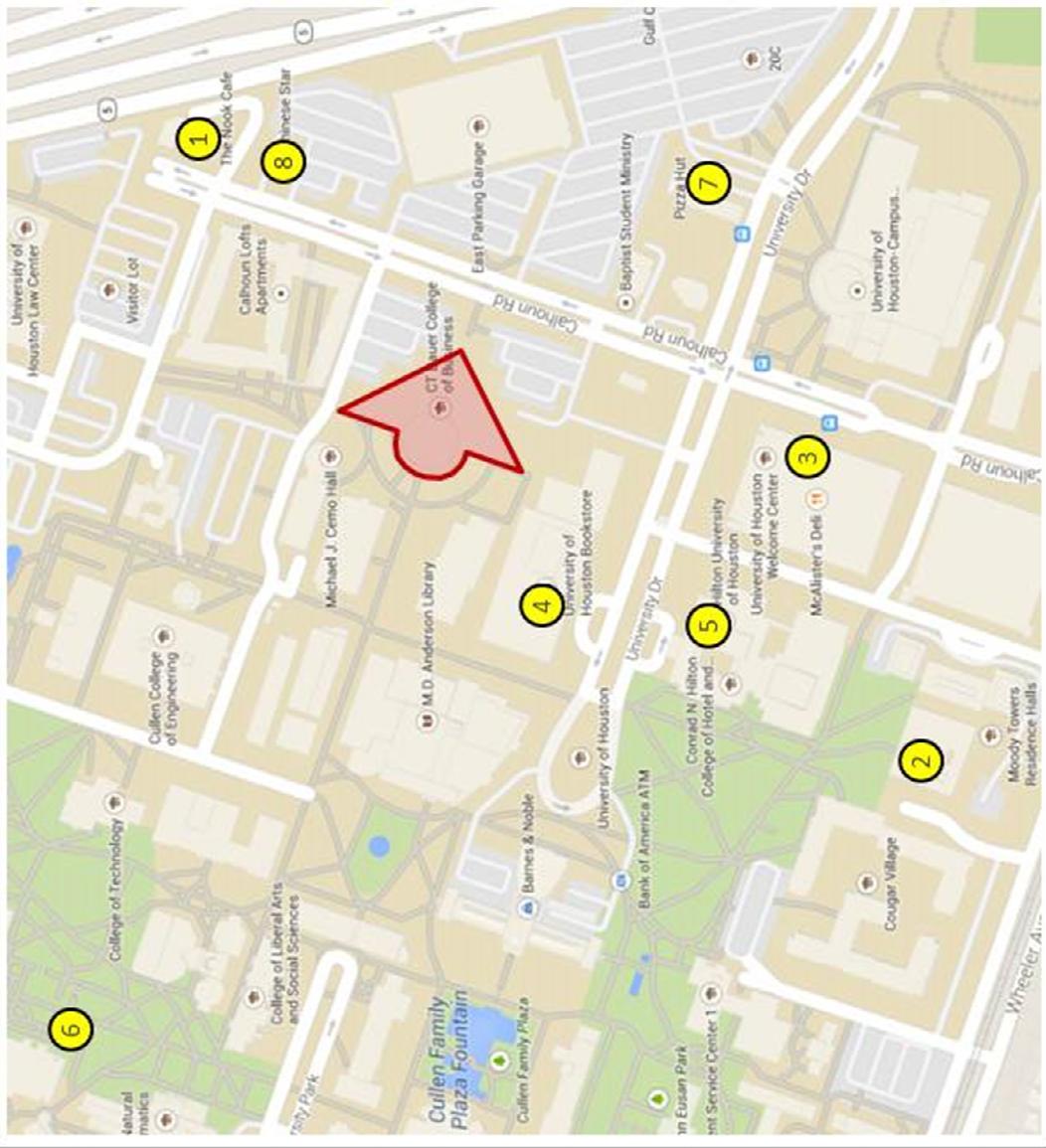
In 1985, the Southwest Catalysis Society was again called on to host a five-day 9th North American Meeting (NAM-9) at Houston's Adam's Mark Hotel. This time, Jack Lunsford and Lynn Slauch were General and Vice Chair; I was Technical Program Chair. Most recently, the SWCS members organized the spectacular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



- ① **Parking garage:** 4400 University Drive, Houston, TX 77204
- ② **Melcher Hall:** building #528
- ★ **Room 160:** symposium and poster site
- walking path from parking garage to SWCS symposium site

LUNCH OPTIONS:

- 1 CAFE 101
PINKS PIZZA
JIMMY JOHNS
(Gourmet Sandwiches)
- 2 MOODY TOWERS
(dining hall, buffet)
- 3 McALISTERS DELI
- 4 STUDENT CENTER
- McDONALDS
- PANDA EXPRESS
- CHICK-FIL-A
- 5 ERIC'S RESTAURANT
(Hilton Hotel)
- 6 UC SATALITE
- PIZZA HUT
- CHICK-FIL-A
- TACO BELL
- BURGER STUDIO
- 7 SUBWAY
- 8 CHINESE STAR



The map shows the University of Houston campus with various buildings and streets. Numbered markers 1 through 8 are placed on the map to indicate the locations of the lunch options listed on the left. A red arrow points to the Student Center area, which is marked with a 4. Other markers include 1 (Cafe 101), 2 (Moody Towers), 3 (McAlister's Deli), 5 (Eric's Restaurant), 6 (UC Satalite), 7 (Subway), and 8 (Chinese Star).