



SOUTHWEST CATALYSIS SOCIETY

2018 FALL SYMPOSIUM

Thursday, December 13, 2018

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Louisiana State University**

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The SWCS officers and I welcome you to the inaugural SWCS Fall Symposium, Thursday, December 13, 2018, in the Historic French House on the campus of Louisiana State University. We hope this event will be an effective venue for academic and industrial catalysis researchers from the region to mix and interact.

We are delighted to present four invited speakers and 21 poster presentations for this year's meeting. Meritorious posters presented by students will be identified with Best Poster Awards with cash prizes.

The 2018 Fall Symposium registration is free for students, \$10 for professionals (online registration), or \$15 (at door). A catered reception will follow the talks by the invited speakers.

Members of SWCS and non-members alike are welcome to participate in this event. We hope to see you at the Symposium!

Ye Xu

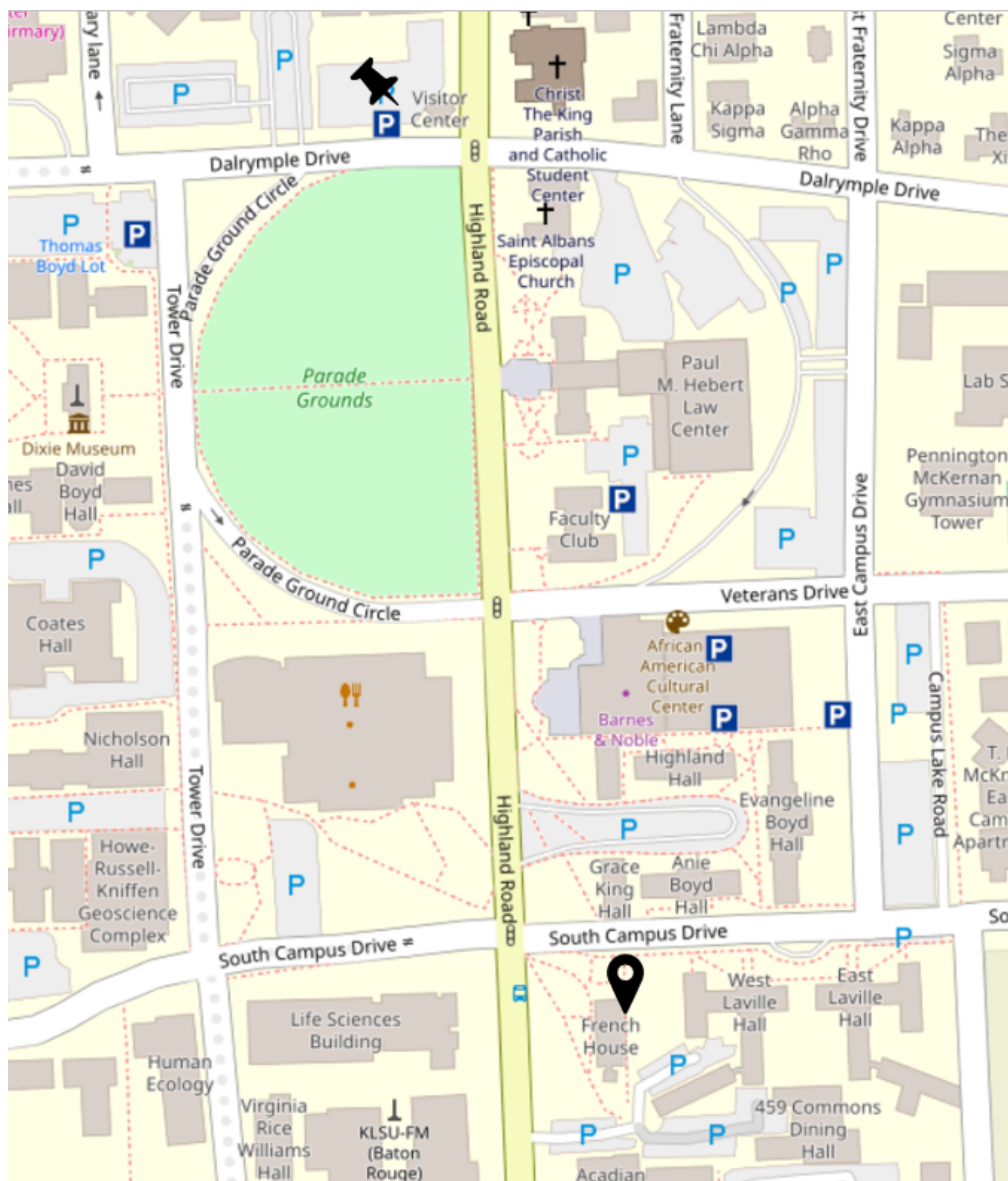
Department of Chemical Engineering
Louisiana State University



2018 FALL PROGRAM

Talks and the poster session will be held in the French House at LSU.

- | | |
|----------------|---|
| 1:00 PM | Registration |
| 1:25 PM | Welcoming Remarks – Ye Xu, Chair |
| 1:30 PM | William J. Layman Jr. , Albemarle Corporation
<i>Hydrocarbon Soluble Saline Hydrides and Their Use in Hydrogen Mediated Saline Hydride Initiated Polymerization</i> |
| 2:10 PM | George G. Stanley , LSU, Department of Chemistry
<i>Highly Active Cationic Cobalt Hydroformylation Catalysts: The Next Industrial Technology?</i> |
| 2:50 PM | Intermission |
| 3:00 PM | Charles Cherry , BASF Corporation
<i>Purification Options for Enhancing and Extending Catalyst Performance</i> |
| 3:40 AM | James J. Spivey , LSU, Department of Chemical Engineering
<i>Direct Conversion of Methane Using Superacids</i> |
| 4:20 PM | Reception (Catered) and Poster Session |
| 5:45 PM | Poster Awards |
| 6:00 PM | Adjourn |



Meeting site – Historic French House (co-ordinates: 30.410916, -91.175548)



Visitor Center



Visitor parking -- <https://www.lsu.edu/parking/parking/visitor.php>

-- Nearest visitor parking: Union Square Parking Garage (behind Barnes & Noble)



Purification Options for Enhancing and Extending Catalyst Performance

Charles E. Cherry, Jr.
BASF Corporation

This talk will address the following topics: 1) Why purify feed streams, including catalyst protection in polymer production processes, extending catalyst run time and improving yield, pre-treatment of monomer and comonomer, and extending catalyst life by minimizing fouling; 2) Processes requiring special feed treatment for polyethylene, polypropylene, and cumene units; 3) Olefin recovery applications requiring feed treatment, including refinery offgas purification, propane dehydrogenation, ethylene and propylene recovery units; 4) Refinery applications requiring treatment, including guard beds for alky beds or reformers, and syngas and acetylene offgas; 5) DeOxo purification; 6) Future trends in adsorbents and catalysts.



Biography

Charles (Chuck) E. Cherry, Jr. is the Global Technology Manager for BASF Corporation, Adsorbent Solutions, where he works closely with colleagues, licensors, researchers and end users to design and develop innovative treatment schemes based on adsorbents. He has a B.S. from the University of Evansville (Evansville, IN) and an MBA from Xavier University (Cincinnati, OH). He has over 39 years' experience in the Adsorption Industry, with increasing responsibilities in Technical, Sales & Marketing management, and celebrated 21 years with BASF (and predecessor companies Alcoa and Engelhard). Chuck is a member of AIChE and ACS and resides in Monument, CO.



Hydrocarbon Soluble Saline Hydrides and Their Use in Hydrogen Mediated Saline Hydride Initiated Polymerization

William J. Layman Jr.
Albemarle Corporation

Low molecular weight anionically polymerized styrene (APS) compositions are of some industrial importance. APS Polymer distributions useful in forming brominated polymeric flame retardants for the electronic enclosure market (computers, television sets, business machines, etc.) have number average molecular weight (M_n) in the range of 500 to about 1300 Daltons. The preparation of such low molecular weight APS composition requires chain transfer mechanisms such that an economic use of alkyl lithium reagents is achieved. Brominated low molecular weight styrenic toluene telomers with bromine contents of 74wt% was introduced to the market as GreenArmor® in 2009 by Albemarle Corporation. Thus, for the GreenArmor process chemistry toluene is the chain transfer agent and styrene is the taxogen. We at Albemarle have recently discovered several new chain transfer processes for the polymerization of styrene wherein hydrogen (H_2) is the chain transfer agent – that is hydrogen mediation of anionic polymerization. These processes entail the use of hydrocarbon soluble saline hydride catalyst to form the hydrogen mediated anionic polystyrene (HMAPS) distributions. The most efficient catalyst for forming HMAPS compositions is formed via hydrogenolysis of Caubère's reagent (Caubère, P. *Chem. Rev.* **1993**, 93, 2317) and represents the first hydrocarbon soluble form of lithium hydride formed and reformed from H_2 . The HMAPS process chemistry, catalysts and finished products will be discussed.



Biography

William J. (Joe) Layman Jr. obtained his undergraduate degree in chemistry from the University of Central Florida (1986), receiving the Graham Baker Award for the Most Outstanding Chemistry Major 1985-1986. His undergraduate research under the guidance of Dr. John T. Gupton (Gupton, J. T., Layman, W. J. *J. Org. Chem.*, **1987**, 52, 3683) entailed the reactions of 2-aryl-3-(*N,N*-dimethylamino)-1-propenes and their corresponding quaternary ammonium salts with organometallic species and reducing agents. He completed his doctoral work at Virginia Tech under the guidance of Dr. James F. Wolf in 1990. His Ph.D. dissertation concerned the " $S_{RN}1$ " reactivity of 2-halobenzene sulfonamides and related compounds (published in part as: Layman *et al.* *J. Org. Chem.*, **2005**, 70, 9147). Joe was hired into Baton Rouge by Ethyl Corporation's Chemicals Group (later spun off as Albemarle Corporation) as a *Senior R&D Chemist* in 1990. In nearly 28 years with Ethyl/Albemarle he has led many projects over a broad spectrum of products and applications serving many markets; among these are: *Biodegradable Detergent Builders*, *Metallocene ligands*, *Pharmaceutical Intermediates*, *Agricultural Actives*; *Phosphine Ligands*, *Phosphorus Flame Retardants*, *Polymeric Brominated Flame Retardants* and *Hydrogen Mediated Anionic Polymerization*. His industrial chemical experience includes 2.5 years plant experience, discovery and process development – as a consequence he has risen to the rank of *Distinguished R&T Advisor*. Joe has 20 US patents with three recently filed additional patents pending, most of which are in the area of environmentally friendly flame retardants and flame retardant synthesis.



Direct Conversion of Methane Using Superacids

James J. Spivey

Department of Chemical Engineering, Louisiana State University

The direct conversion of methane to higher-value is of significant catalytic interest. Examples include aromatization and oxidation coupling, among others. The use of superacids to oligomerize methane was the subject of Olah's Nobel Prize. His catalysts were liquid $\text{SbF}_5\text{-HSO}_3\text{F}$ and $\text{SbF}_5\text{-HF}$, which rapidly deactivated in the presence of hydrogen. Other attempts to develop gas and solid superacids have been reported. For example, recent work at LSU has shown that gas-phase $\text{AlBr}_3\text{-HBr}$ is a superacid for methane oligomerization. However, the complex product mixture of unreacted methane, hydrogen, higher hydrocarbons, and Br-based hydrocarbons was difficult to fully characterize. A solid superacid would be of interest, and there is little literature on solid superacids for methane oligomerization. We are aware of only sulfated zirconia for this reaction. Here, we demonstrate a solid superacid for this reaction, based on a heterogeneous analog of the gas phase $\text{AlBr}_3\text{/HBr}$.



Biography

Jerry Spivey is James Shiver Professor at LSU. His education includes BS and MS at NC State and PhD at LSU. His research has focused on hydrocarbon conversion, syngas catalysis, and clean fuels. He is the author of more than 200 publications and editor of more than 30 books. He is also Editor-in-Chief of *Catalysis Today* and Editor of the *Catalysis SPR* book series (Royal Society of Chemistry, Cambridge UK).



Highly Active Cationic Cobalt Hydroformylation Catalysts: The Next Industrial Technology?

George G. Stanley

Louisiana State University, Department of Chemistry

A new class of highly active cationic cobalt(II) bisphosphine hydroformylation catalysts will be discussed. They are hundreds of times more active than the known industrial cobalt catalysts: $\text{HCo}(\text{CO})_4$ and $\text{HCo}(\text{CO})_3(\text{PR}_3)$. These catalysts have the general form: $[\text{HCo}(\text{CO})_x(\text{P}_2)](\text{BF}_4)$, where $x = 1-3$, and P_2 = chelating bisphosphine. Unlike all other hydroformylation catalysts this new class has a positive order on the CO pressure, that is, they run faster with higher pressures of CO. Unlike rhodium hydroformylation catalysts, these catalysts are remarkably resistant to cobalt-induced phosphine ligand degradation reactions and are capable of extremely high turnover numbers (e.g., one million). The high activity of these catalysts allow them to operate under lower temperatures and pressures relative to $\text{HCo}(\text{CO})_4$ and $\text{HCo}(\text{CO})_3(\text{PR}_3)$. These cationic Co(II) catalysts are very active at alkene isomerization, similar to neutral cobalt hydroformylation catalysts. They are especially effective at hydroformylating internal branched alkenes to produce linear aldehydes. Comparisons with rhodium catalysts and $\text{HCo}(\text{CO})_4$ will be presented.



Biography

George Stanley received his B.S. in Chemistry from the University of Rochester (1975, senior research with Rich Eisenberg), Ph.D with F. Albert Cotton at Texas A&M University (1979), and was a NATO & CNRS Postdoctoral Fellow with John Osborn at the Université Louis Pasteur in Strasbourg, France (1979-81). He started his academic career in 1981 at Washington University in St. Louis. In 1986 he moved to Louisiana State University in Baton Rouge where he is currently the *Cyril & Tutta Vetter Alumni Professor of Chemistry*. George chaired the Inorganic Chemistry Gordon Research Conference in 2005 and was Chair of the Organometallic subdivision of the Inorganic Chemistry division of the ACS in 2009. He is currently Chair of the Industrial & Engineering Chemistry (IEC) division of ACS. Society honors include ACS Fellow (2011) and AAAS Fellow (2014). George's research interests traditionally involved bimetallic cooperativity in homogeneous catalysis, but the discovery of a highly active monometallic cationic cobalt(II) hydroformylation catalyst with commercial applications has refocused his efforts on this new system.



POSTER ABSTRACTS

1. Ternary Oxides for Dry Reforming of Methane: Rapid Screening of Rare-Earth – Transition Metal Catalysts and Sulfur Tolerance Evaluation

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

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The purpose of this work is to acquire a “proof of principle” data set towards the development of sulfur- and water tolerant (especially the former) transition metal-doped rare-earth oxysulfide (TM-REO) catalysts for high temperature reforming, and develop a mechanistic rationale for how surface sulfidation alters reforming and coke formation kinetics. Experimental reactivity studies using feeds characteristic of methane dry reforming are used to identify doped TM-REO (e.g., Ni/Ce-Zr) systems that can be tolerant of sulfur and water at realistic levels, an extension of our previous work on tar reforming. To date, we have tested many different metal/REO combinations (Ni, Mn, Co, Fe, Pd, Ru, W)-doped Ce/La and Ce/Zr catalysts at 725-775°C for dry reforming (1:1 CH₄:CO₂) and combined dry/steam reforming (1:1 CH₄:CO₂ but with water added). Many of these tests were performed using a TGA/DSC method we developed to simultaneously and rapidly measure dry reforming and coking rates. Some of the better catalysts were further evaluated in the presence of 0.07 ppm and 20 ppm (in the feed) of sulfur (fed as dimethylsulfoxide). Used catalysts have to date been characterized by Raman spectroscopy, XRD, CO chemisorption, and XPS.



2. Catalytic Research Characterization Capabilities: CAMD Synchrotron Facility

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The Center for Advanced Microstructures and Devices (CAMD), is one of seven synchrotron light sources in the nation, and the only light source of its kind in the South. The heart of CAMD is a 1.3 GeV electron storage ring producing synchrotron radiation from the infrared, to hard X-rays. The spectral brightness of synchrotron radiation makes it ideal to study a broad range of material and chemical properties of catalytic systems. Analytical techniques include i) soft and hard X-ray absorption spectroscopy; ii) X-ray diffractometry; iii) small angle X-ray scattering; iv) photoemission spectroscopy. The K and L absorption edges of elements (near edge X-ray absorption fine structure (NEXAFS)) in the range 200 eV to 1000 eV can be measured at the varied line space plane grating monochromator beamline. X-ray absorption spectroscopic measurements (X-ray absorption near edge structure spectroscopy (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS)) can be routinely made for elements from silicon upward in the periodic table at the Lexus (Low Energy X-ray) and Hexas (High Energy X-ray) beamlines spanning the ranges 1.8 keV to 10 keV and 5 keV to 30 keV, respectively. A wide range of detectors are available for fluorescence measurements at low concentrations. *In situ* experiments can be conducted with different types of cells, such as Lytle cells. Powder diffraction can be conducted in Bragg-Brentanno and Debye Scherrer modes at three beamlines. Two four-circle Huber goniometers are available for this type of experiment. A new small angle scattering (SAXS) beamline will facilitate longer-range structural characterization of a wide variety of solid and liquids, such as colloids, polymers, macromolecules. Pilatus 300R and MAR165 CCD detectors are available for two-dimensional measurements. Anomalous X-ray diffraction (with the X-ray energy above and below an absorption edge of interest) can be conducted. Low-energy (20 – 150 eV) photoemission spectroscopy is available to directly probe the valance properties of materials.



3. Synthesis of Mesoporous Metal Oxides - An Example for Undergraduate Research

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Ceria have been suggested to be superior supports for catalytic reactions such as water-gas shift reaction, in tuning CO/H₂ ratio in syngas. It also has the added benefit of not being toxic to living things, as well as more readily available than other lanthanides. Mesoporous ceria is more appealing due to their tunable structure and pore size. The hard template nanocasting method is applied to synthesize mesoporous ceria with ordered structure. KIT-6 was used as a template and the cerium nitrate was the precursor, followed by calcination. The mesoporous ceria was then characterized by BET analysis to determine the surface area, TEM for nanostructures, and RAMAN spectrometry for the crystallinity. The results confirm that mesoporous metal oxide-ceria has been successfully synthesized. This work is mainly performed by undergraduate students.



4. Influence of the Structure Directing Agent Isomer of Zeolite SSZ-39 on the Selective Catalytic Reduction of Nitric Oxide

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Small pore zeolites such as SSZ-39 have shown great promise as catalysts for methanol to olefins and SCR.¹ SSZ-39 can be synthesized in a straightforward manner with N,N-dimethyl-3,5-dimethylpiperidinium as the structure directing agent, which is available in a cis and trans form. Our lab has previously reported that varying the cis/trans ratio of the SDA impacts the aluminum content of the resulting zeolite as well as the synthesis kinetics.² Recently we have found that the SDA cis/trans ratio also impacts the catalytic activity of NO_x SCR, particularly at high temperature (>450 °C) and low temperature (<250 °C) data points. Presented will be SCR data with SSZ-39 synthesized with varying SDA cis/trans isomer ratios along with zeolite characterization.

(1) Dusselier, M., Schmidt, J.E., Moulton, R., Haymore, B., Hellums, M., et al. *Chem. of Materials* 27, 7 (2015).

(2) Ransom, R., Coote, J., Moulton, R., Gao, F., Shantz, D.F. *Ind. Eng. Chem. Res.*, 56 (2017).



5. Steam-Assisted Crystallized Fe-ZSM-5 Materials and Their Unprecedented Activity in Benzene Hydroxylation to Phenol Using Hydrogen Peroxide

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

A series of Fe-ZSM-5 samples with steam-assisted crystallization (SAC) and conventional methods were successfully synthesized. All the characterizations (PXRD, FE-SEM, UV-Vis, In-Situ IR, etc.) related to these catalysts are presented. It has been shown that due to much less diffusion resistance, stability, and enhanced H₂O₂ activation, the hierarchical samples show superior performance over the microporous Fe-ZSM-5 materials in benzene oxidation at mild conditions. The best synthesized sample gives conversion of 25.5% with phenol selectivity of 90% after 8 hours, corresponding to TON of 82. At the similar conditions, TS-1 (Si/Ti molar ratio of 50) catalyst indicates 1.1 % benzene conversion and 63% phenol selectivity after 4 hours. These encouraging results show SAC samples have potential to be used as solid catalysts in benzene hydroxylation to phenol.

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

(1) L. Balducci, D. Bianchi, R. Bortolo, R. D'Aloisio, M. Ricci, G. Spanò, R. Tassinari, C. Tonini, R. Ungarelli, *Adv. Synth. Catal.* 349 (2007) 979–986.

(2) J. He, H. Ma, Z. Guo, D.G. Evans, X. Duan, *Top. Catal.* 22 (2003) 41–51.

(3) J. He, W.P. Xu, D.G. Evans, X. Duan, C.Y. Li, *Microporous Mesoporous Mater.* 44-45 (2001) 581–586.

(4) J. Li, C. Zhou, H. Xie, Z. Ge, L. Yuan, X. Li, *J. Nat. Gas Chem.* 15 (2006) 164–177.



6. Controlling the Concentration of Oxygen Vacancies via Spatial Tailoring of the Active Sites in Homogeneously Dispersed Nanoparticles

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According to Environmental Protection Agency, over 55% of NO_x production in the US is caused by automobile exhaust, also resulting in the formation of CO₂ and hydrocarbon residues. Transition metal doped CeO₂-ZrO₂ (CZO) nanoparticles (NPs) are extensively employed in three-way catalysis due to their ability to adsorb and release oxygen helping to prevent coking. These CZO NPs have shown catalytic activity comparable to state of the art catalysts utilized in dry reforming of methane. However, the activity of these structures under reaction conditions, which is function of the active site (Ni) dispersion, has been shown to reduce the oxygen storage capacity and increase coking over time. To address this, the current work aims to understand the structural and atomic properties of CZO NPs by homogeneously dispersing the active sites (Ni) to investigate the stability, catalytic activity, and increased lattice strain.

In this work, a two-step process, co-precipitation/molten salt synthesis (MSS), has been explored for a CZO:Ni catalyst, comparing its catalytic activity and oxygen vacancy concentration to a standard prepared by sol-gel technique. Transmission electron microscopy and X-ray diffraction identify that the as-synthesized NPs are monodisperse spheres, with diameters between 10-20 nm, exhibiting fluorite phase. The endothermic energy associated with the dry reforming of methane was extracted via DSC, resulting in comparable values for this synthesis (up to 7.1 mW/mg) compared to the sol-gel method (8.46 mW/mg) despite their reduced initial surface area at 33 m²/g compared to 60-70 m²/g for the sol-gel synthesis. The concentration of oxygen vacancies in these NPs was studied using Raman spectroscopy, which shows a higher intensity defect-induced (D) band at 600 cm⁻¹ for the as-synthesized catalyst than the reported standard. Furthermore, to evaluate the concentration of oxygen vacancies in the lattice, spatial correlation model was used to estimate the defect (oxygen vacancy) concentrations versus grain size of the NPs to compare to results obtained from Raman spectroscopy. These preliminary results on CZO:Ni catalysts demonstrate that active site dispersion will enable the ability to control the oxygen vacancies in the lattice which is the first step to understand the diffusion of the active site during a reaction.



7. Photo-Reactivity of a Dioxo Mo(VI) Complex towards C–H Activation for C–C Bond Formation

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Metal oxos are key intermediates in a variety of catalytic processes relevant to both biological and industrial processes. Typically, late transition metal oxos are used due to their thermodynamic instability and high reactivity. However, these same characteristics have also made mechanism studies challenging and hindered the development of structure/activity relationships that are important to rationally optimize the catalysis. Herein, an alternative approach is taken where stable early transition metal oxos are prepared and high energy excited electronic states are generated to initiate reactivity. The photo-reactivity of a molybdenum dioxo complex bearing a bipyridine ligand is investigated to gain insight into its electronic excited state reactivity towards different substrates. The reactivity of this excited state species, unlike the ground states of it and analogue molecules towards oxidation of the olefins (O-atom transfer) is found to readily C–H activate a variety of substrates. This reactivity can be attributed to its excited state as opposed to its ground state, which did not show any reactivity in O-atom transfer to the olefins or activating the C–H bonds (based on GCMS data). Based on the observation of this model system which falls in the concept of uphill catalysis, one would be able to study a vast number of photo-generated reactive excited state species which are quite stable, almost unreactive and easy to handle as their ground state under ambient conditions, which can be of great importance in developing photocatalytic transformations.



8. Mixed Metal Small Pore Zeolites: Synthesis, Characterization and Catalytic Testing

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Metal-exchanged zeolites have found a range of industrial applications due to the imparting of d-block metal functionality into the uniform confined spaces of the zeolite micropores. As an example, copper-exchanged high-silica chabazite has emerged as the industrial catalyst of choice in the selective catalytic reduction (SCR) of NO. Thus, while there have been many studies of single metals exchanged into zeolites, the case of mixed transition metal zeolites obtained is very sparse. This work will outline our initial efforts to exchange two metals into SSZ-13 and their properties.

SSZ-13 with Si/Al ratio of 15 was used for the synthesis of various d-block metal exchanged zeolites. Cobalt, nickel and zinc were chosen for this study due to the similarity of their electronic structure to that of copper. Single d-block transition metal and mixed transition metal SSZ-13 were prepared using copper and other metals stated. Mixed metal zeolites were synthesized titrating copper SSZ-13 samples to achieve second extra-framework transition metal cation concentrations of 25%, 50% and 75%.

The NO SCR activities of metal-exchanged zeolites were examined using a packed bed flow system. The current work will present synthesis and characterization results of mixed metal zeolites. NO conversion and N₂O formation results for mixed metal SSZ-13 as a function of temperature will be shown.



9. A Three-step Reaction to Produce Fuel from Oxygenates via Multifunctional Catalysts

Yueyun Lou and Daniel F. Shantz*

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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.



10. Amine Functionalized OMS as Model Materials for Aqueous Acid 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 bound 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, the binding process at the molecular level was probed using pulsed-field gradient NMR. To do this, particles of interest must be small enough (<10 nm) to be observable and be a stable colloid for the duration of the measurement. The synthesis, amine grafting, and phase transfer is shown to obtain aqueous colloidal silica nanoparticles as well as information on the overall governing mechanisms of the process. Preliminary results are also shown for solution NMR experiments utilizing these particles for acetic acid separation. Additionally, this method is not only limited to separations and could be utilized to probe amine-catalyzed reactions and potentially any reaction on a functionalized silica surface.



11. Quinone-Modified Ligands as Proton-Coupled-Electron-Transfer Relays for Catalysis

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Quinone motifs offer a well-defined 2-electron and 2-proton equilibrium that can be exploited to store reducing equivalents in the hydroquinone form. Additional modification of the quinone-functionality provides a method to control the hydroquinone/quinone equilibrium and thus the thermodynamics associated with the transfer of the reducing equivalents. Overall, similar to the use of pendant acid relays, it is hypothesized that the pendant quinones can act as a highly variable PCET relay for lowering activation barriers and improving electro-catalyst efficiencies.¹ Progress has already been made towards the synthesis of quinone-functionalized ligands. Initially, several amine-substituted quinones were prepared and characterized. Preliminary studies have indicated a poor binding affinity of these monodentate ligands. As a result, our ligand design strategy has been altered to include various bidentate motifs. Two initial targets include bipyridyl and β -diketiminato ligands. There are two primary benefits of this direction: (1), the chelate effect of these bidentate ligand scaffolds should greatly improve the binding affinity relative to the initial amino-quinones that have been studied; (2) these ligands can be easily functionalized to affect the redox properties of the complex. This will allow the redox properties of the overall complex to be tuned to optimize the complex to be more efficient at mediating the PCET events and improving relevant catalytic performances.

(1) PNAS. **2014**, 111, 42, 15005.



12. Dirhodium Tetraphosphine 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, H_2 , and CO. The dirhodium catalyst, $[Rh_2(\mu-CO)(CO)_3(rac\text{-}et,ph\text{-}P4\text{-}Ph)](BF_4)_2$, is highly active leading to favorable results when using a DMF/water solvent system, 1-hexene, 90 psi 1:1 H_2 /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, $[Rh_2(nbd)_2(rac\text{-}et,ph\text{-}P4\text{-}P4)](BF_4)_2$ (nbd = norbornadiene). My research has focused on the synthesis of new dirhodium catalyst precursors that avoid the problems associated with the norbornadiene complex. Our current hypothesis is that the norbornadiene complex is too sterically hindered to allow facile displacement of the norbornadiene ligand by CO. A second problem is that the norbornadiene can re-coordinate and inhibit the catalyst. New catalyst precursors with acetonitrile, pyridine, and cyclooctadiene ligands show good activity for hydroformylation in water/acetone solvent. *In-situ* FT-IR and NMR experiments were performed on the bimetallic catalyst to understand the active catalyst and mechanism for the catalytic cycle.



13. Coupling of Acetaldehyde to Crotonaldehyde on $\text{CeO}_{2-x}(\text{111})$

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Selective C-C coupling of oxygenates is pertinent to the manufacture of fuel and chemical products based on sustainable energy technologies such as biomass conversion and CO_2 reduction. Here we report a combined experimental and theoretical study on the temperature-programmed reaction (TPR) of acetaldehyde (AcH) on a partially reduced $\text{CeO}_{2-x}(\text{111})$ thin film surface. The experiments were carried out under ultra-high vacuum conditions without continuous gas exposure, allowing better isolation of active sites and reactive intermediates than in flow reactor conditions. AcH does not undergo aldol condensation in a typical TPR procedure,¹ even though the enolate form of AcH (CH_2CHO) is readily produced on $\text{CeO}_{2-x}(\text{111})$.² We find however that a tailored “double-ramp” TPR procedure is able to successfully produce an aldol adduct, crotonaldehyde (CrA). Using DFT calculations and microkinetic modeling we explore several possible C-C coupling pathways. We conclude that the double-ramp procedure produces surface oxygen vacancy dimers stabilized by adsorbate occupation that is dynamically formed during the TPR. The vacancy dimers enable C-C coupling to occur between an enolate and an adjacent AcH molecule. The proposed mechanism suggests that CrA desorption is rate-limiting while C-C coupling is facile.³

(1) Chen, T.L.; Mullins, D.R.; *J. Phys. Chem. C* 115 (2011) 3385-3392.

(2) Calaza, F.C.; Xu, Y.; Mullins, D.R.; Overbury, S.H.; *J. Am. Chem. Soc.* 134 (2012) 18034-18045.

(3) Zhao, C. et al.; *J. Phys. Chem. C* 10.1021/acs.jpcc.8b08535



14. Hydrogen Production from the Steam Reforming of LPG over Supported Perovskites.

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In this work LaNiO_3 perovskites-type precursors were characterized and had their performances evaluated during the steam reforming of LPG to produce hydrogen. Three precursors were synthesized: a non-supported perovskite (LaNi), a supported perovskite on Al_2O_3 (LaNi/AL) and a supported perovskite on $\text{CeO}_2\text{-SiO}_2$ (LaNi/CS). *In situ* XRD analyses indicated that all samples were successfully reduced at 700 °C, except for LaNi/AL . This result was ascribed to NiAl_2O_4 and $\text{LaNi}_{0.5}\text{Al}_{0.5}\text{O}_3$ phases observed on this sample, which might have granted a high thermal stability to the precursor. TPR and XANES tests indicated that the unsupported perovskite had lower reduction temperatures than the supported ones which shows a clear influence of the supports in the thermal stability of the catalysts. The steam reforming of LPG was performed at 600 °C, during 24 h in order to analyze the catalytic activity of each sample. It was observed that the non-supported perovskite presented an initial conversion of 35% but deactivated after only 5 hours of reaction, probably due to carbon deposition. LaNi/CS had an average initial LPG conversion of 40%, but after 24 h of reaction the conversion dropped to 20%. Coke might also have been the main responsible for the progressive deactivation observed, despite the oxygen mobility of the support which helps the gasification of deposited carbon. Average LPG conversion was 55% for LaNi/AL , which was the most active catalyst, probably due to a better Ni dispersion obtained for this sample. TGA tests were performed after the stability tests and confirmed coke deposition over all catalysts especially on LaNi that showed the highest carbon formation rate.



15. Controlling Catalytic Reaction Pathways via Magnetic Heating

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The catalysis market is responsible for more than 35% of the world's GDP, and it is involved in the most successful industrial sectors: energy generation, chemicals, and pharmaceuticals. Despite the remarkable advances in catalytic technologies, the industry still faces thermal management issues and accumulation of heat on reactor walls. Alternatively, it is possible to overcome the activation barrier using *in situ* methods via iron oxide (Fe_3O_4) exposed to an alternating magnetic field. In this work, Fe_3O_4 nanoparticles will be used to convert alternating magnetic fields to heat to study the effects of localized energy on the chemical transformation in a reference alcohol condensation reaction.

In this work, 20 nm iron oxide nanoparticle spheres, cubes, and truncated octahedrons of tunable sizes are exposed to RF fields to drive an alcohol dehydration reaction. The size and shape of these particles are controlled by varying surfactant to precursor ratio in thermal decomposition reactions. These facets allow for the tuning of surface activity and heat generation, key parameters for selectivity and activity engineering. The heat generated is dependent on the spin configuration on the surface, with minimum heating rates at least 34% higher than commercially available particles. Surface functionalization with hydroxyl groups is performed to increase the interaction of Fe_3O_4 with alcohols in dehydrogenation reactions. This localized heat generation can be used to control surface functionalization for dispersion in aqueous solutions and conversion of alcohols. For spherical particles, the GC-MS data shows production of aldehydes and esters via thermal routes while RF induced reactions result in longer alkenes, such as decene, which is dependent on the applied magnetic field. These results indicate changes in the reaction mechanism associated with RF activation. Furthermore, to investigate the role of the surface of iron oxide without any surfactants on the mechanism of the reaction, spherical nanoparticles are also synthesized via co-precipitation routes. The catalyst is characterized before and after functionalization and reaction steps to probe the crystal structure, alcohol physisorption and morphology of the particles, using XRD, Inelastic Neutron Scattering (INS), and HRTEM respectively. The reaction products are characterized via GC-MS to elucidate the reaction mechanism.



16. Engineering the Dopant Position in the Host Lattice for Modified Photocatalytic Properties

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Transition metal (TM) doped semiconductor materials are extensively employed for light harvesting and photocatalytic applications owing to their increased light absorption and charge mobility. In this work, spatial tailoring of the Ni position in TiO₂ nanostructures is performed by varying the secondary processing parameters (drying and annealing) to engineer the resulting optoelectronic properties for select applications. Highly doped TiO₂:Ni²⁺ (15 mol %) nanoparticles (NPs) were synthesized via sol-gel chemistry. The aging of the dried Ti sol was observed to be a moisture sensitive phenomenon, resulting in segregation of hydroxylated Ni clusters. FTIR and time-resolved UV-Vis absorption spectroscopy confirmed the interaction of atmospheric moisture with the dopant in the dried sol. After annealing, a clear NiO phase segregation was observed for the aged and annealed powders from XRD and HRTEM-EELS characterizations. Additionally, TGA-DSC measurements demonstrated the substitution of the ethoxy group with ambient moisture, resulting in the ejection of the hydroxylated Ni clusters. Furthermore, the effect of annealing rate on dopant position was studied by rapidly annealing the dried sol. Rapid annealing locks the dopants in the host lattice, quenching the doped system into a metastable state. Similar trend of dopant segregation and dopant incorporation was observed with other first row TM doped TiO₂ powders. Finally, the photocatalytic activity of these different TiO₂:Ni²⁺ NPs under AM 1.5G solar light highlights the relationship between the recombination kinetics and the dopant position. This ability to spatially control the dopant position in highly doped materials allows for direct control of specific optoelectronic properties, which will assist in the development of solar cells, photocatalytic devices, etc.



17. Elevated Temperature Adsorptive Desulfurization of JP-8 with High Sulfur Concentration Using Metal Exchanged Zeolite Y

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Adsorptive desulfurization of liquid fuels has been widely investigated for remote electricity generation with fuel cells. Despite its high efficacy for model fuels, room temperature adsorptive desulfurization is still not efficient for real complex fuels containing high concentrations of sulfur. The use of elevated temperatures in this process may allow for increase in sulfur selectivity by stimulating the displacement of competing hydrocarbon species while still retaining sulfur compounds. However, adsorptive desulfurization at elevated temperatures has not been sufficiently investigated in the literature. In this work, we perform adsorptive desulfurization with Cu-exchanged Na-Y zeolite (CuNa-Y) in batch reactors at temperatures between 30°C and 180°C with JP-8 fuel containing 2,230ppmw sulfur. The results show that increasing the temperature of adsorption corresponds to an increase in the amount of sulfur removed in JP-8 from 2.5mg-S/g-adsorbent at 30°C to 36mg-S/g-adsorbent at 180°C. Desulfurization experiments with model fuel representations of JP-8 containing 3-methylbenzothiophene in n-dodecane with and without toluene show that the sulfur adsorption is dependent on temperature and that sulfur removal comprises the contribution of weak adsorption (on Na sites and on Cu sites at low temperatures – 30°C and 80°C) and strong adsorption (on Cu sites at elevated temperatures - 130°C and 180°C). Weak adsorption is suitable for desulfurization only for the model fuel and in the absence of competing aromatic species. Strong adsorption, formed by chemical reaction of Cu sites in the zeolite and 3-MBT at adsorption temperature $\geq 130^\circ\text{C}$, as shown in our temperature-programmed desorption experiments with TGA-MS, leads to improvement in sulfur removal by CuNa-Y zeolite in a real JP-8 sample. The experiments suggest that competing compounds may be partially displaced by sulfur compounds at these elevated temperatures. In adsorptive desulfurization with metal-exchanged zeolites, utilizing elevated temperatures presents opportunity for improved efficacy and possible future commercialization of such process.



18. Gas Chromatography Study of Sulfur Removal from Jet Fuel Using CuNa-Y Zeolite

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Adsorptive desulfurization has been studied as a promising process to produce low-sulfur liquid fuels that achieve more stringent regulations. Although the process has proved to be effective to remove sulfur compounds from liquid fuels, a deep understanding of how the desulfurization occurs is still missing. In this work, gas chromatography coupled with Pulsed Flame Photometric Detector, GC-PFPD, is used to analyze the sulfur content of JP-8 samples before and after adsorptive desulfurization using Cu-exchanged Na-Y zeolite (CuNa-Y) at different temperatures. The aim of the work is to investigate if the adsorptive removal is selective to a certain fraction of sulfur compounds in the matrix of JP-8. Also, the effect of temperature on the sulfur removal is studied.



19. Theoretical Investigation of the Adsorption of Phosphate Monoesters on CeO₂(111)

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The ability of ceria to catalyze the dephosphorylation reaction¹ has recently gained attention for purposes of remediating harmful organophosphates and reclaiming phosphorous. As an initial step in exploring the kinetics of this reaction, the adsorption of model phosphate monoesters, including phosphoric acid, methyl phosphate, and para-nitro phenyl phosphate (*p*-NPP), at various sites of CeO₂(111) is studied in detail using density functional theory calculations. The bonding of the monoesters to surface lattice oxygen, O²⁻ via phosphorous atom (P-O_{latt}) is preferred over the adsorption to Ce⁴⁺ sites via phosphoryl oxygen atom, on the stoichiometric ceria surface. Partial reduction of the surface, characterized by oxygen vacancies, adsorbed hydrogen atoms, or Ce³⁺ species, did not enhance the adsorption. Calculated minimum energy profiles for the dephosphorylation of methyl phosphate and *p*-NPP suggest that the P-O_{latt} adsorption mode activates the P-O ester bond so that it readily dissociates. The hydration of the residual HPO₃ group and desorption of phosphoric acid, on the other hand, are found to be rate-limiting.²

(1) Manto, M. J.; Xie, P.; Wang, C.; *ACS Catal.* 7 (2017) 1931–1938.

(2) Zhao, C.; Xu, Y.; *Catal. Today* 312 (2018) 141-148.

20. Podand-Based Siloxide Ligands as a Scaffold for Molybdenum Catalyzed Alkyne Metathesis: The Role of Ligand Flexibility in Catalyst Activity and Lifetime

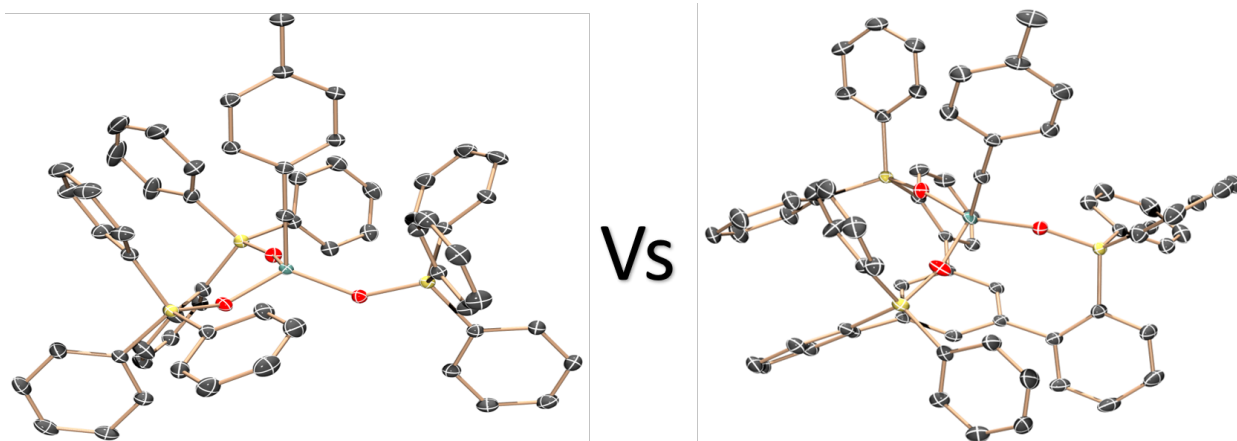
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Olefin metathesis is a well-developed and indispensable tool in organic and organometallic chemistry, and few of the known catalysts have reached the ubiquity and success enjoyed by the carbenes of Schrock or Grubbs. On the other hand, alkyne metathesis has been less developed relative to its olefin analog and the catalysts associated with it have been largely relegated to serving niche roles in synthetic methodology. The lone exception to this are the tris-triphenylsiloxide supported molybdenum alkylidyne complexes reported by Furstner and Moore which have nearly unrivaled activity, functional-group tolerance and in certain instances, catalyze cross-metathesis with terminal alkynes. With that said, there still exist conditions and/or functional-groups in which this class of catalysts fail and so refinement of ligand design remains a crucial step for improving performance. Herein we report the chelating siloxide ligand, $\text{C}_6\text{H}_3(\text{C}_6\text{H}_4\text{SiPh}_2\text{O})_3$, whose structural rigidity allows for the characterization of well-defined alkylidyne complexes and whose reduction in activity relative to the $-\text{OSiPh}_3$ derivative, despite having a reduced steric profile, suggests that ligand flexibility is another crucial aspect of design for alkyne metathesis catalysts as well as giving a direct and empirical comparison on the role the Si-O-Mo bond angle has on activity.





21. Nitrate Anions Degrade Rapidly on Indium-Decorated Pd Nanocubes

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Bimetallic indium-decorated palladium nanoparticles (In-on-Pd NPs) are active for the room-temperature catalytic reduction of nitrate anions in water, in which the active sites are ensembles of metallic In atoms distributed across the Pd surface.¹ The Pd NPs are pseudo-spherical in shape, and it is unclear if their faceted nature plays a role in nitrate reduction. Here we synthesized cube-shaped Pd NPs with different edge lengths and with different In surface coverages (sc%), and studied the resulting In-on-Pd nanocubes (NCs) for nitrate reduction. The NCs exhibited volcano-shape activity dependence on In surface coverage, with peak activity near 65, 75, and 66 sc% for NCs with edge lengths of 11, 18, and 23 nm, respectively. When rate constants are normalized to the most coordinatively unsaturated surface atoms (i.e., edge and corner atoms), all NCs are ~20-fold more active than In-on-Pd nanospheres, with maximum activity correlated to 4 to 5 In atoms per 10 Pd edge/corner atoms. These results suggest In atoms are more active for nitrate reduction when associated with Pd cube edge/corner atoms, which can be the basis for improving bimetallic catalysts for water denitrification and other hydrogenation reactions.

(1) Guo, S. et al.; *ACS Catalysis*. 52 (2018) 503-515.



22. Enhancing Cobalt Based Hydroformylation with a Cationic Catalyst

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Hydroformylation is a widely used industrial process to produce aldehydes from alkenes, H_2 , and CO . Interest in cobalt based hydroformylation technologies has dwindled for several decades now with rhodium based technologies stealing most of the spotlight. We hope to change that with the development of a new class of cobalt catalyst based on a cationic metal center and chelating phosphine ligands. With high turnovers, fast rates, and moderate reaction conditions this class of catalyst has the potential to outshine rhodium based technologies for some select processes. Examples of product distributions with different alkenes under varied reaction conditions are reported. Additionally comparisons to industrial catalyst are made.



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).**