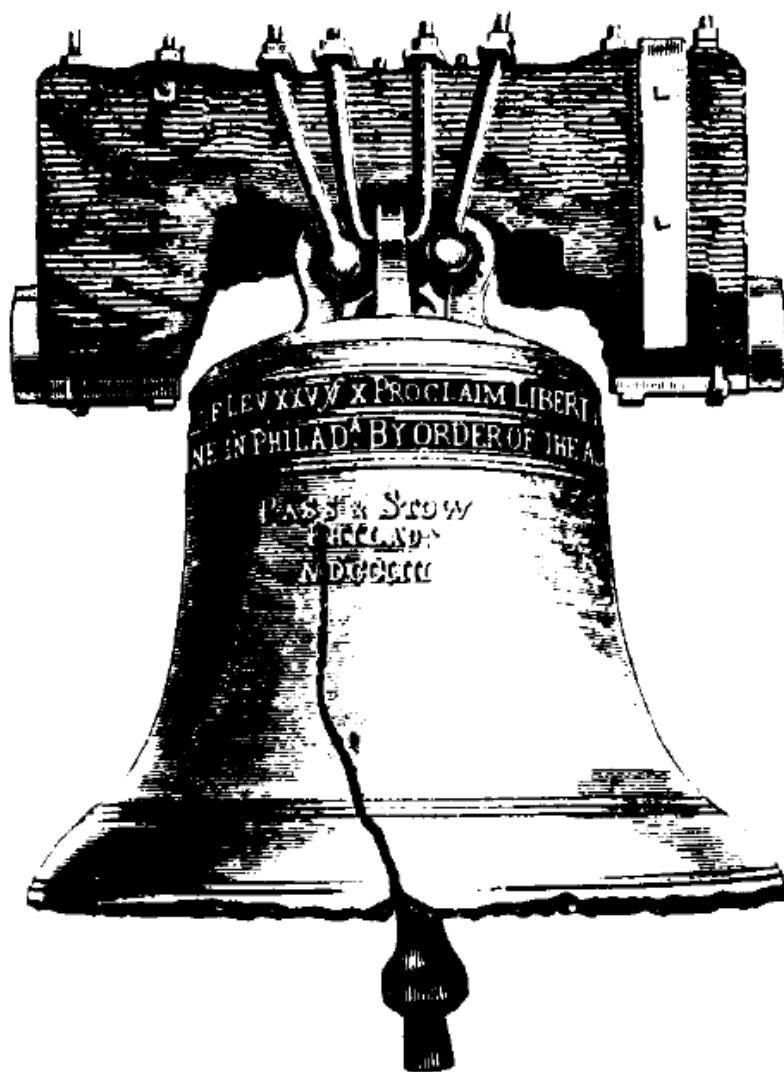


Catalysis Club of Philadelphia

2018 Spring Symposium Abstracts



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**Thursday, May 17, 2018
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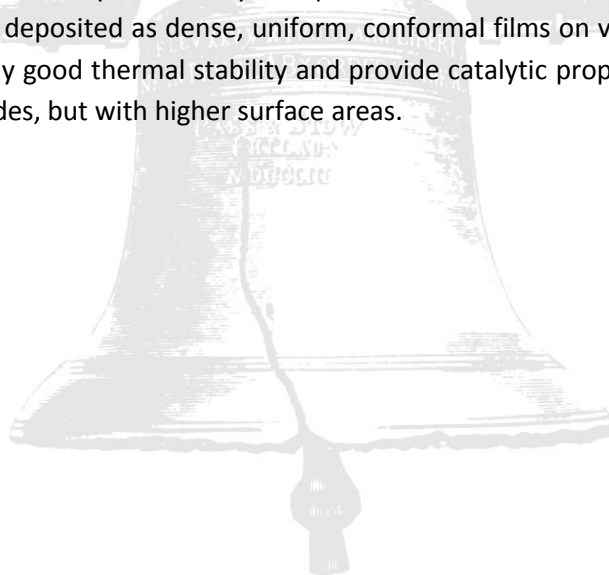
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Fabrication of Nano-Structured Catalyst Supports by ALD

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Interactions between a transition-metal catalyst and its support can strongly alter the stability and activity of the catalyst. Important examples include support effects with ceria and the so-called “Intelligent Catalysts” in which the metal can be redispersed by reversible exsolution from a perovskite lattice. However, the surface areas of these functional supports are often too low or unstable; and, in the case of perovskites, the length scales for ingress and egress may be too long to take advantage of the effect. We are addressing these issues by depositing very thin films of various functional oxides, ~0.5 to 2 nm thick, onto high-surface-area supports, including Al_2O_3 and MgAl_2O_4 , by Atomic Layer Deposition. We have demonstrated that a wide range of oxides can be deposited as dense, uniform, conformal films on various supports. The films exhibit surprisingly good thermal stability and provide catalytic properties similar to that observed with bulk oxides, but with higher surface areas.



Influence of Confining Environment Polarity on Ethanol Dehydration Catalysis by Lewis Acid Zeolites

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The different reactivity of Lewis acid sites (M) in zeolite frameworks, when confined within non-polar (hydrophobic) or polar (hydrophilic) secondary environments, can arise from differences in competitive inhibition by solvents,¹ solvent-mediated mechanisms,² and extended solvent structures.³ Framework Lewis acid centers also adopt open ((HO)-M-(OSi≡)₃) and closed (M-(OSi≡)₄) configurations that show different reactivity for Baeyer-Villiger oxidation,⁴ glucose isomerization,³ and aldol condensation.⁵ Here, we interrogate the reactivity of Sn centers isolated within Beta zeolites using bimolecular ethanol dehydration to diethyl ether (404 K). Sn sites in open and closed configurations, quantified from IR spectra of adsorbed CD₃CN before and after reaction, convert to structurally similar intermediates during ethanol dehydration catalysis (404 K) and revert to their initial configurations after regenerative oxidation treatments (21% O₂, 803 K). Dehydration rates (404 K, 0.5–35 kPa C₂H₅OH, 0.1–50 kPa H₂O) measured on ten low-defect (Sn-Beta-F) and high-defect (Sn-Beta-OH) zeolites were described by a rate equation derived from mechanisms identified by DFT calculations,⁶ and simplified using microkinetic modeling to identify kinetically-relevant pathways and intermediates. Polar hydroxyl defect groups located in confining environments preferentially stabilize reactive (ethanol-ethanol) and inhibitory (ethanol-water) dimeric intermediates over monomeric ethanol intermediates. As a result, equilibrium constants (404 K) for ethanol-water and ethanol-ethanol dimer formation are 3–4× higher on Sn-Beta-OH than on Sn-Beta-F, consistent with insights from single-component and two-component adsorption measurements. Intrinsic dehydration rate constants (404 K) were identical among Sn-Beta-OH and Sn-Beta-F zeolites; thus, measured differences in dehydration turnover rates solely reflect differences in prevalent surface coverages of inhibitory and reactive dimeric intermediates at active Sn sites. The confinement of Lewis acidic binding sites within secondary environments of different defect density confers the ability to discriminate surface intermediates on the basis of polarity, providing a design strategy to accelerate turnover rates and suppress inhibition by water.

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Low temperature NO_x storage on zeolite supported Pd for low temperature diesel engine emission control

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Recent legislation requirements have turned controlling NO_x emissions into one of the biggest technical challenges facing car manufacturers [1]. At present, the main technologies available for this application are NO_x storage and reduction (NSR) or urea based selective catalytic reduction (SCR) [2,3]. Both technologies can achieve high NO_x reduction efficiencies once they reach their operating temperature (typically 200°C or higher). During cold start, when the exhaust temperature is below 200°C, both systems are less efficient at NO_x removal.

To meet the NO_x emission standards during the cold start (<200°C) a new concept has been introduced: passive NO_x adsorbers (PNA) [4]. These are materials which store NO_x (mainly as NO) at low temperatures and then thermally release the stored NO_x once the downstream NO_x reduction catalyst (NSR or SCR) reaches its operating temperature.

This contribution will report the remarkable ability of zeolite supported Pd to store NO with very high trapping efficiency at temperatures below 200°C and conditions that simulate real exhaust from diesel engines. The study will focus on the characterization of the Pd storage sites on zeolites compared to oxide supports and understanding unique nature of the active species in these materials. The properties of palladium supported on three different zeolites of various pore sizes (CHA, MFI and BETA) will be compared to classical oxidic supports (Al₂O₃ and CeO₂).

Also, with the aim of providing insight into the behaviour of these materials during engine operation, the evolution of the NO storage sites under various gas feed compositions has been probed through combined “operando” IR and XAS experiments. The findings of these study will be discussed in relation to the realistic operation of the novel PNA technology.

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Mechanisms, active intermediates, and descriptors for epoxidation rates and selectivities on dispersed early transition metals

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Early transition metal atoms (groups IV-VI) dispersed on silica and substituted into zeolites effectively catalyze the epoxidation of alkenes with hydrogen peroxide or alkyl peroxide reactants, yet the underlying properties that determine the selectivities and turnover rates of these catalysts are unclear. Here, a combination of kinetic, thermodynamic, and in situ spectroscopic measurements show that when group IV - VI transition metals are dispersed on silica or substituted into zeolite *BEA, the metals that form the most electrophilic sites give greater selectivities and rates for the desired epoxidation pathway and present smaller enthalpic barriers for both epoxidation and H₂O₂ decomposition reactions.

In situ UV-vis spectroscopy shows that these group IV and V materials activate H₂O₂ to form pools of hydroperoxide and peroxide intermediates. Time-resolved UV-vis measurements and the isomeric distributions of *cis*-stilbene epoxidation products suggest that the active species for epoxidations on group IV and V transition metals are only M-OOH and M-(O₂)²⁻ species, respectively. Mechanistic interpretations of turnover rates show that these group IV and V materials catalyze epoxidations (e.g., of cyclohexene, styrene, and 1-octene) and H₂O₂ decomposition through similar mechanisms that involve the irreversible activation of coordinated H₂O₂ followed by reaction with an olefin or H₂O₂. Epoxidation rates and selectivities vary over five- and two-orders of magnitude, respectively, among these catalysts and depend exponentially on both the energy for ligand-to-metal charge transfer (LMCT) and chemical probes of the difference in Lewis acid strength between metal centers. Together, these observations show that more electrophilic active-oxygen species (i.e., lower-energy LMCT) are more reactive and selective for epoxidations of electron-rich olefins. The micropores of zeolites about active sites can serve to preferentially stabilize reactive states that lead to epoxidations by changing the mean diameter of the pore or the density of nearby silanol groups. Consequently, these properties provide opportunities to increase rates of epoxide formation over that within mesoporous silicas. Consistently, H₂O₂ decomposition rates possess a weaker dependence on the electrophilicity of the active sites and the surrounding pore environment, which indicates that catalysts with both greater rates and selectivities may be designed following these structure-function relationships.

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Commercial Perspective of Alternative Routes to Acrylic Acid Monomer

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Acrylic acid and corresponding acrylates are major monomers for a variety of functional polymers used broadly in our daily life such as coating, sealant, and personal care. The two-stage selective oxidation of propylene to acrolein and then to acrylic acid was first commercialized in early 70s and quickly became the dominant route to acrylic acid. Driven by feedstock cost or availability or sustainability, significant efforts from both industry and academia were devoted to developing alternative routes to acrylic acid. Catalyst plays critical role in the key step of transforming different raw material into product effectively, for example, mixed metal oxides MoVTenbOx in propane selective oxidation, solid acids in dehydration of glycerin or 3-HP, and various oxides in aldol condensation of acetic acid and formaldehyde. This presentation will discuss the progress of these major routes, the challenges towards commercialization, and potential solutions.



Tuning the Electrocatalytic Oxygen Reduction Reaction Activity of PtCo Nanocrystals by Cobalt Concentration and Phase Transformation Methods

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The proton exchange membrane fuel cell (PEMFC) is a critical technology to enhance the clean, sustainable production and usage of energy, but practical application remains challenging because of the high cost and low durability of the cathode catalysts that perform oxygen reduction reaction (ORR). Efforts have been placed on the study of introducing first-row transition metals in Pt-M alloys to reduce the Pt loading and modulate geometric, structural and electronic effects. To further improve the ORR reaction rate and catalysts stability, alloys that adopt an intermetallic structure, especially the tetragonal L1₀-PtM phase, has been one of the most promising materials. In this contribution, monodisperse PtCo nanocrystals (NCs) with well-defined size and Co composition are synthesized *via* solvothermal methods. The transformation from face-centered cubic (fcc) to ordered face-centered tetragonal (fct) structure was achieved *via* thermal annealing. Depending on the selection of transformation methods, different degrees of ordering were introduced and further correlated with their ORR performance. A detailed study of the annealing temperature and composition dependent degree of ordering is also highlighted. This work provides the insight of discovering the optimal spatial distributions of the elements at the atomic level to achieve enhanced ORR activity and stability.

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

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

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Using Water as a Co-catalyst in Heterogeneous Catalysis to Improve Activity and Selectivity

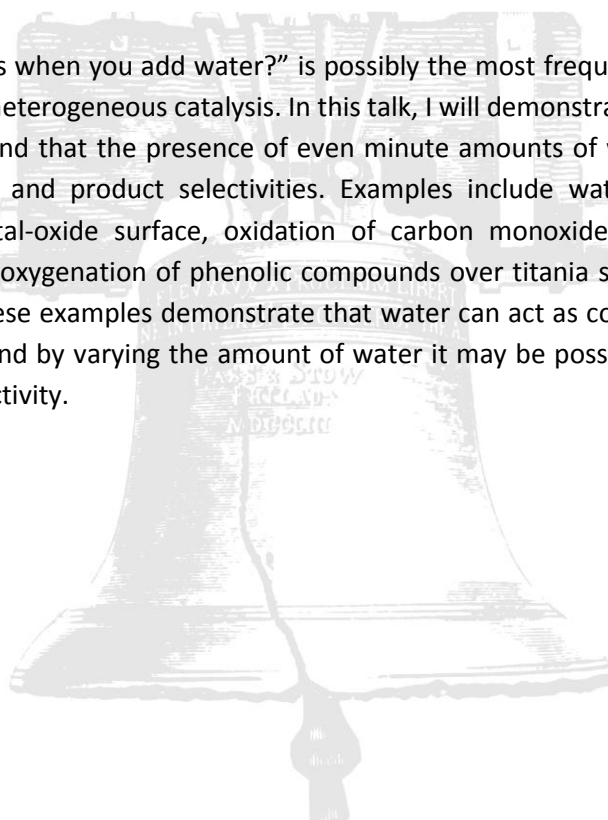
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“What happens when you add water?” is possibly the most frequently asked question after presentations in heterogeneous catalysis. In this talk, I will demonstrate that this question is indeed paramount and that the presence of even minute amounts of water can drastically change reaction rates and product selectivities. Examples include water-mediated proton hopping across a metal-oxide surface, oxidation of carbon monoxide at the gold/titania interface, and hydrodeoxygenation of phenolic compounds over titania supported ruthenium catalysts. Together, these examples demonstrate that water can act as co-catalyst in a variety of catalytic reactions and by varying the amount of water it may be possible to tune reaction rates and product selectivity.



Renewable Isoprene By Sequential Hydrogenation of Itaconic Acid and Dehydra-Decyclization of 3-Methyl-Tetrahydrofuran

Omar Abdelrahman

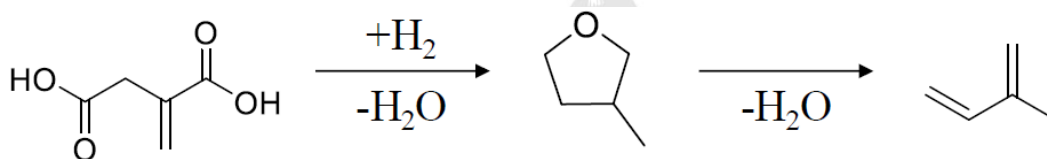
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The catalytic conversion of biomass-derived feedstocks to value added chemicals is an important challenge to alleviate the dependence on petroleum-based resources. To accomplish this, the inherently high oxygen content of biomass compounds, such as that of lignocellulosic biomass, requires significant reduction via hydrodeoxygenation strategies. The unsaturated carboxylic acid itaconic acid (IA) can be produced from biomass via fermentation pathways, for example. A pathway of interest is the conversion of IA to isoprene, facilitating the renewable production of an industrially relevant diolefin. IA can be successively hydrogenated to yield 3-methyl tetrahydrofuran (3-MTHF), in a one-pot cascade reaction, where a Pd-Re bimetallic catalyst results in an 80% yield to 3-MTHF. The 3-MTHF can then be converted to isoprene, and other pentadienes, through an acid catalyzed vapor-phase dehydra-decyclization. Multiple solid acid catalysts, including aluminosilicates, metal oxides and phosphorous modified zeolites, were screened for the dehydra-decyclization step. A new class of catalytic materials, all silicon phosphorous containing zeolites, were found to be the most selective (70% isoprene and 20% pentadienes), where the major side reaction involved is a retro-prins condensation of 3-MTHF to butane and formaldehyde. Through kinetic studies, an investigation into the effect of Brønsted acid strength, pore size and operating conditions on the selectivity to isoprene are discussed. The prospect of applying this dehydra-decyclization strategy to other saturated cyclic ethers will also be discussed, which enables the production of other diolefin molecules of interest such as butadiene and linear pentadienes.



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