

2019 Pacific Coast Catalysis Society Meeting

August 9, 2019



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PCCS Schedule

August 8, 2019

3:00 pm to 5:00 pm: Optional Tour of the Voiland School of Chemical Engineering and Bioengineering in **Wegner Hall** with Billy Schmuck.

August 9, 2019

Smith Center for Undergraduate Education (CUE) 202

7:15 am-8:00 am: Registration and Breakfast

Morning Session 1.

Chair: Jean-Sabin McEwen (Washington State University)

8:00 am – 8:10 am: Welcome from Pres. Kirk Schulz

8:10 am – 8:45 am: Susannah L. Scott, *Nuclearity Effects in Supported Zinc and Gallium Catalysts for Alkane Dehydrogenation*

8:45 am – 8:50 am: Discussion

8:50 am – 9:25 am: Ya-Huei (Cathy) Chin, *Catalytic Cycles for Activating Light Alkanes on Transition Metal and Metal-Oxide Catalysts*

9:25 am – 9:30 am: Discussion

9:30 am – 10:05 am: *6-Minute Poster Presentations (Samantha Bennett, Jacob Bray, Kristin Bryant, Greg Collinge, Kyle Groden)*

10:05 am – 10:35 am: Coffee Break

Morning Session 2.

Chair: Su Ha (Washington State University)

10:35 am – 10:52 am: Kandis Leslie Abdul-Aziz, *Elucidating the Design Rules for Smart “Geo-Inspired” Catalysts*

10:52 am – 10:55 am: Discussion

10:55 am – 11:30 am: Roger Rousseau, *Catalyst Design for Electrochemical Hydrogenation of Organic Compounds*

11:30 am – 11:35 am: Discussion

11:35 am – 12:15 pm: *6-Minute Poster Presentations (Ellis Hammond-Pereira, Nicholas Jaegers, Konstantin Khivantsev, Fan Lin, Luke Minardi, Bo Peng)*

12:15 pm – 1:45 pm: Lunch and Poster Session. **Posters in CUE Atrium.**

Afternoon Session 1.

Chair: Líney Árnadóttir (Oregon State University)

1:45 pm – 2:02 pm: Zdenek Dohnálek, *Mechanistic Understanding of the Formic Acid Adsorption and Reaction on Anatase TiO₂(101)*

2:02 pm – 2:05 pm: Discussion

2:05 pm – 2:40 pm: Francisco Zaera, *New Nanostructures for Increased Selectivity and Stability in Catalysis*

2:40 pm – 2:45 pm: Discussion

2:45 pm – 3:02 pm: Tej S. Choksi, *On the Bottom-up Design of Bimetallic Catalytic Nanoparticles with Atomic Level Resolution*

3:02 pm – 3:05 pm: Discussion

3:05 pm – 3:40 pm: Manh Thuong Nguyen, *Novel Single-Atom Catalysts: Insights from Experiment and Large Scale Molecular Simulations*

3:40 pm – 3:45 pm: Discussion

3:45 pm – 4:25 pm *6-Minute Poster Presentations (Andrew Raub, Manish Shetty, Verena Streibel, Nisa Ulumuddin, Austin Winkelman, Borna Zandkarimi).*

4:25 pm – 4:50 Coffee Break

Afternoon Session 2.

Chair: Steven Saunders (Washington State University)

4:50 pm – 5:25 pm: Abhaya K. Datye, *Atom Trapping: Key to the Design of Thermally Stable and Regenerable Catalysts*

5:25 pm – 5:30 pm: Discussion

5:30 pm – 6:00 pm Break

6:00 pm – 8:30 pm Conference Dinner.

Dinner in Elson S. Floyd Cultural Center: <https://culturalcenter.wsu.edu>.

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Catalytic Cycles for Activating Light Alkanes on Transition Metal and Metal-Oxide Catalysts

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The selective dehydrogenation of alkanes to alkenes is an important process in the valorization of shale gas liquids and in the production of on-demand olefins. Ga- and Zn-modified aluminosilicates have been extensively studied as catalysts for these reactions. In the presence of Brønsted acid sites (BAS), the olefins undergo subsequent aromatization to more valuable BTX. The nuclearity of the metal active sites, the proximity between the metal sites and the BAS, and the nature of the support, may influence the catalytic activity but detailed structure-property relationships are difficult to ascertain in conventional catalysts with many types of sites. The reactions of GaMe₃ and ZnMe₂ with the hydroxyl-terminated surfaces of dehydrated silica and alumina, as well as with the internal and external surfaces of H-ZSM-5, are particularly simple. They generate methane and isolated dimethylgallium and methylzinc sites.^{1,2} K-edge X-ray absorption spectra, analyzed via inspection of the wavelet transform EXAFS (WT-EXAFS) and curvefitting of the Fourier transform EXAFS (FT-EXAFS), reveal that the silica and zeolite materials contain dinuclear grafted sites, regardless of the thermal pretreatment of the support, while alumina gives dispersed mononuclear grafted sites.³ Differences in reactivity and stability appear to originate in these structural variations.⁴

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Catalytic Cycles for Activating Light Alkanes on Transition Metal and Metal-Oxide Catalysts

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Most catalytic turnovers require multiple elementary catalytic steps, which occur sequentially, to complete a single molecular sojourn. Often, active site identities and the requirements differ among these steps. For a specific reaction, the key to designing an active catalyst depends on the requirements of the molecule to overcome the kinetic bottleneck, which changes with changing identity of the kinetically relevant step. We present a concept of rationalizing the various, concomitant catalytic cycles in light alkane (C1 and C2) conversion, and then describe the design of catalysts with multiple types of active sites on transition metal and metal oxide catalysts, which assemble together to promote the desired catalytic cycle while suppressing the undesired cycle to attain the overall catalyst stabilities and yield.

Described within this talk is the concept of kinetic couplings, the connection between thermodynamics and kinetics, and the dynamic transition of active site structures during C1 and C2 alkane activation, capturing the events of carbon deposition, oxidation of reactive intermediates, and removal of coke. Methane catalysis with O₂ produces CO₂ and H₂O, while with a much softer oxidant of CO₂ or H₂O produces syngas on late transition metal catalysts (Ni, Pt, Pd, etc.). Ethane catalysis also gives similar products, but on early transition metal catalysts, its reaction with O₂, CO₂, and H₂O leads also to ethylene, as a valuable precursor for synthesizing commodity chemicals and polymers. These reactions occur via the kinetic coupling of the alkane activation and the oxidation of the alkane derived intermediates, which include the reactive intermediates and precursors for coke formation. By deciphering the kinetically coupled catalytic cycles, together with the concomitant catalytic path that leads to coke deposition, we can then design active site structures that interject the cycle for coke deposition. Blending a more oxophilic transition metal (e.g., Co, Fe) into transition metals (e.g., Ni) increases the surface concentration of reactive oxygen; these oxygen adatoms alter the C-H bond activation paths in alkane, by directly assisting with the C-H bond activation step, they also scavenge the carbonaceous intermediates and increase their removal rates. For the case of ethane oxidation, doping a more effective metal into transition metal oxides (e.g., Co in MoO_x/Al₂O₃) increases the rates of co-reactant (CO₂) activation, which then increases the carbon oxidation rates, removing the strongly bound carbon species, thus freeing up active sites.

These catalytic cycles and their coupling dictate the rates and selectivities of the alkane conversion reactions, and understanding them, followed by promoting the desired catalytic cycles, while interjecting the undesired cycles would lead to stable and effective catalysts.

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Catalyst design for electrochemical hydrogenation of organic compounds

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The hydrogenation of organic molecules offers a way to combine renewable electrical energy and chemical conversions with an eye towards storing electrical energy in high energy chemical bonds or enabling distributed processing of waste carbon, such as biomass and waste water sludges, into chemicals and fuels. Nevertheless, a critical mechanistic understanding of how these processes work is still lacking. Hence, our ability to optimize and control electrochemical transformations of organic molecules is also limited.

In this context, we will discuss how atomistic simulations are shaping our current mechanistic understanding of the electrocatalytic hydrogenation of organic molecules. We identify two main routes: (i) The first, via a Langmuir-Hinshelwood mechanism, requires that both the hydrogen and organic be on the electrode surface; (ii) The second, via an Eley-Rideal mechanism, requires that only the organic compounds reside on the metal surface, and hydrogenation occurs via a proton coupled electron transfer. The nature of the mechanisms depends on the metal, the external potential and the pH. However, irrespective of the route, binding of the organic to the surface and competition for surface sites with hydrogen are key parameters. These two ingredients form a basis for rapid screening of electrocatalyst for a desired conversion and will be illustrated by a combination of modelling and experimental results.

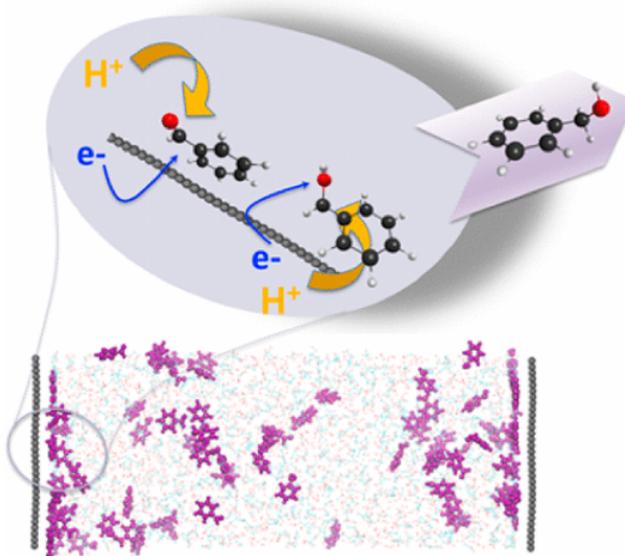


Figure 1. Atomistic simulations reveal a picture of molecular speciation on the electrode surface.

New Nanostructures for Increased Selectivity and Stability in Catalysis

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One of the major challenges in heterogeneous catalysis is the preparation of highly selective and robust catalysts. The goal is to be able to synthesize solids with stable surfaces containing a large number of specific surface sites designed for the promotion of a particular reaction. New synergies between surface-science studies and novel nanosynthesis methodology promise to afford new ways to design such highly selective catalysts in a controlled way. In this presentation we will provide a progress report on a couple of projects ongoing in our laboratory based on this approach. Platinum-based catalysts have been prepared for the selective trans-to-cis conversion of olefins, with a design based on early surface-science work with model surfaces and quantum mechanical calculations that indicated a particular preference for (111) facets in promoting the formation of the cis isomers. We are currently extending this research by using the concept of "single-site catalysis" with Pt-Cu bimetallics for the selective hydrogenation of unsaturated aldehydes. In a second example, new metal@TiO₂ yolk-shell nanomaterials conceived for both regular and photo-induced catalytic applications have been used to promote CO oxidation at cryogenic temperatures and to suggest that in photocatalysis the role of the metal may not be to scavenge the excited electrons produced in the semiconductor upon absorption of light, as commonly believed, but rather to promote the recombination of the adsorbed atomic hydrogen initially produced by reduction of H⁺ on the surface of that semiconductor. New mixed-oxide surfaces are being designed using atomic layer deposition (ALD) as well.

Novel Single-Atom Catalysts: Insights from Experiment and Large Scale Molecular Simulations

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Addressing the challenges of renewable source and clean energy has become a critical priority for the global economy, where processes like hydrogen separation, or CO₂ hydrogenation. It has been recognized that in such processes, hydrogen activation [1] over heterolytic catalysts, metal dispersion [2,3] and type of supports [4] play a very important role in determining the activity and selectivity of the catalysts. Supported single atom catalysts (SAC) [5] represent a novel area of research in this direction. Critical knowledge gaps are: synthesis control and stability of SACs, density and sinter-resistant sites, how the differ from traditional supported nano-particles.

In this presentation, I will discuss the mechanism of H₂ adsorption, dissociation and H spillover of Pd SACs on reconstructed Fe₃O₄(001) using STM and DFT calculations, demonstrating the effect of support reducibility on hydrogen activation and charge transfer.

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Atom Trapping: Key to the Design of Thermally Stable and Regenerable Catalysts

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Heterogeneous catalysts represent the mainstay of the chemical industry, and a large majority involve nanoparticles on a support. Decreasing size of the nanoparticles leads to better utilization of the precious metals, with the highest atom efficiency being achieved when the metal is atomically dispersed in the form of isolated atoms. Isolated atoms become mobile at elevated temperatures, causing agglomeration into nanoparticles. Our research is focused on developing methods to control the growth of particle size and the transformation of nanoparticles into isolated single atoms [1-3].

Supports differ in their ability to maintain small particles. The figure below shows STEM images of three catalysts that contain 1 wt% Pt synthesized using the same amine precursor. The catalysts were all calcined at 500 °C in air to decompose the precursor. It is evident that very different sized Pt particles are formed. The ceria support contains isolated Pt atoms, the alumina support shows sub-nanometer sized particles while the MgAl₂O₄ support shows larger particles. The conventional term used to describe these differences is metal-support interactions (MSI), which is meant to suggest bonding of the metal nanoparticle with the oxide support. But the term MSI fails to capture the underlying mechanism that leads to these observations.

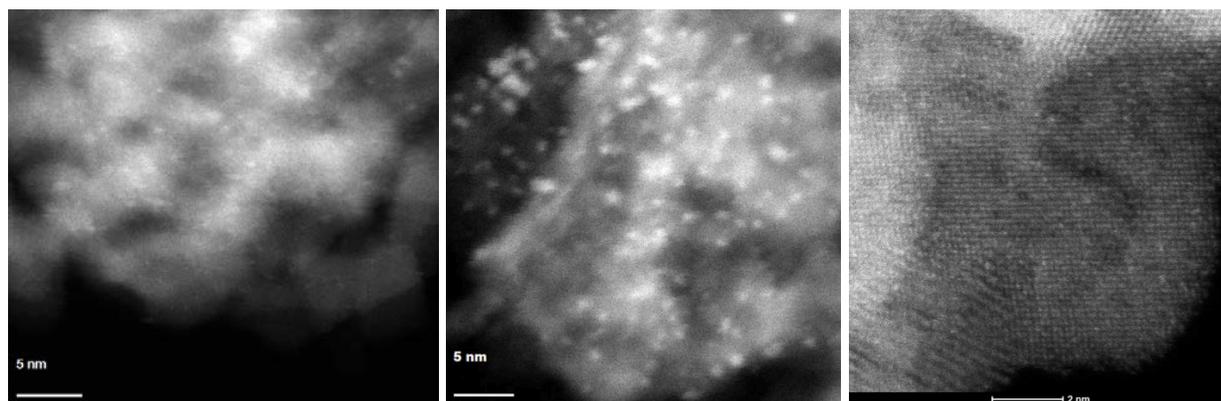


Figure 1. HAADF STEM images of 1wt%Pt on La-Al₂O₃ (left), MgAl₂O₄ (center) and CeO₂ (right) after impregnation, drying and calcination at 550°C/4h. The resulting Pt particle sizes are very different.

We have characterized these differences in catalyst supports in terms of their ability to trap atoms. We learnt that ceria supports help generate a stable and fully regenerable Pt catalyst that can change reversibly from single atoms into metallic nanoparticles [3]. The understanding of atom trapping derived from ceria supports can be translated to other oxide supports. This will impact not only automotive exhaust treatment (where catalysts are exposed to high temperature) but also other industrial reactions such as propane dehydrogenation or methane oxidation, where high temperatures are required. The presentation will focus on the understanding of atom trapping and its application for design of thermally stable and regenerable catalysts.

Atom Trapping: Key to the Design of Thermally Stable and Regenerable Catalysts

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Elucidating the Design Rules for Smart “Geo-Inspired” Catalysts

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A significant concentration of point defects in the bulk of perovskites is associated with inducing a dynamic response to the surrounding environment [1]. This dynamic response has been utilized by the heterogeneous catalysis and solid-oxide fuel cell community to develop a sort of smart or intelligent “geo-inspired” catalysts [2,3]. For example, LaFeO₃, when reduced at elevated temperatures, exsolves excess B-site cations and/or dopant atoms as nanoparticles on the surface. Subsequent exposure to an oxidizing environment reverses the exsolution process and the nanoparticles dissolve back into the lattice. The exsolved nanoparticles have a strong interaction with the perovskite support that can be described as “socketing” or grooves on the surface [4]. Our laboratory has discovered that defect engineering imposes design rules for controlling the dispersion and chemical composition of exsolved nanoparticles. This poster will present insight on the driving force behind the exsolution of Ni nanoparticles from LaMnO₃ and LaFeO₃. The LaFeO₃ and LaMnO₃ support was defect engineered with either La or Fe vacancies. The size of the nanoparticles observed were much larger with supports containing La vacancies. Alloying of the exsolved Ni nanoparticles occurred at elevated temperatures above 700 °C. The support effects are elucidated for understanding possible controls for the rational design of “geo-inspired” catalysts.

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On the Bottom-up Design of Bimetallic Catalytic Nanoparticles with Atomic Level Resolution

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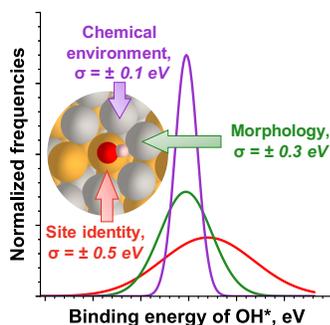
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The advent of increasingly sophisticated density functional theory (DFT) derived workflows has transformed designing bimetallic alloy catalysts from an Edisonian endeavor into one guided by descriptor-based design principles. Recent advances notwithstanding, prevailing catalyst design paradigms remain limited by two key features. First, these paradigms use idealized models based on extended surfaces to describe nanoparticles encompassing diverse shapes, compositions, and sizes. These assumptions create a materials gap between model structures and catalytic architectures under reaction conditions. Second, it remains a formidable endeavor to precisely tailor structural and compositional features of active sites motifs while ensuring the stability of active sites during working conditions.

We address these knowledge gaps using robust property \Rightarrow structure workflows [1 - 4] that screen binding energies of catalytic descriptors with atomic level resolution while concurrently determining stabilities of active site motifs on-the-fly. Site stabilities (BE_{site}) are predicted using our coordination-based alloy stability model [1, 2] while binding strengths of catalytic descriptors (BE_{ads}) are determined through a new-class of site-specific scaling relations [3, 4]. Our workflow is inspired by the “near-sightedness” of itinerant d-electrons which efficiently screens structural and compositional perturbations beyond the first coordination shell of an adsorption site.



Despite the remarkably limited parameter space, our paradigm predicts BE_{ads} and BE_{site} with accuracies of 0.10-0.15 eV for bimetallic nanoparticles having diverse shapes (cubo-octahedral, decahedral, icosahedral, and octahedral), sizes (greater than 1.6 nm), compositions (binary pairings of 30 transition and post-transition metals), bulk crystal structures (fcc, bcc, hcp, and tetragonal), and under applied strain ($\pm 3\%$). By propagating site-specific scaling relations through microkinetic models of probe reactions like CO oxidation and NO reduction, we interrogate the effect of structural and compositional features of active site ensembles on catalytic turnovers with site-by-site resolution.

Figure 1: Deconstructing adsorption sites in bimetallic alloys.

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Mechanistic Understanding of the Formic Acid Adsorption and Reaction on Anatase TiO₂(101)

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The adsorption of small molecules on the surfaces of metal oxide catalysts, particularly TiO₂ as a prototype, is of great interest from the view of fundamental adsorption properties and catalytic behavior. Here we focus on the interactions of formic acid, the simplest carboxylic acid, with anatase TiO₂(101) surface using a combination of scanning tunneling microscopy (STM), infrared reflection absorption spectroscopy (IRRAS), and temperature programmed desorption (TPD). This combination of techniques allows us to follow the surface intermediates and products as a function of reaction conditions in unprecedented detail. At lower temperatures (< 300 K) we focus on understanding the competitive binding via molecular monodentate and deprotonated bidentate species as a function of coverage and temperature. The density of surface hydroxyl, originating from deprotonation of formic acid, starts to decrease above 400 K in accord with the appearance of a broad water TPD peak at 450 K. The desorption of water coincides with the emergence of a new C-containing intermediate with three distinct adsorption configurations. We speculate that this intermediate is a result of bidentate reactions with surface oxygen vacancies created by water formation and desorption. This intermediate subsequently yields carbon monoxide and formaldehyde products above 550 K, as revealed by TPD. These studies provide the first experimental account of formic acid reactions on model anatase TiO₂(101) surface and complement prior extensive investigations on rutile TiO₂(110).

Dual reaction pathways of CO hydrogenation toward methane over various supported cobalt catalysts

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Catalytic conversion of a mixture of hydrogen and carbon monoxide according to Fischer-Tropsch synthesis (FTS) produces methane, hydrocarbons, and oxygenates. In spite of the fact that a range of short and long hydrocarbons can be synthesized in high pressure FTS, methane is the most favored product thermodynamically. Various groups have tried to understand the mechanism of methane formation^{1,2}, however, no congruent view has been reached so far. The present paper will inspect the nature of the different “carbon pools” frequently involved in mechanistic studies of methane formation.

We have developed Chemical Transient Kinetics (CTK) to study the mechanism of methane formation via CO hydrogenation. The CTK method implies a switching from a H₂ equilibrated catalyst surface to reactive H₂/CO conditions. This causes the catalytically active phase to be formed (build-up). Conversely, once the steady-state is reached, a back-transient can be initiated by switching back to H₂. This process is monitored as a function of time by a mass spectrometer. Surface coverages can be calculated based on surface atom counting. In the present study, CTK has been used at different H₂/CO ratios over Co/SiO₂, Co/TiO_x, and Co/MnO_x catalysts to understand the mechanism of methane formation.

Our results show that two mechanisms, at least, are responsible for methane formation. At very early stages of the reaction, when the catalyst surface provides metallic sites, a (hydrogen-assisted) CO dissociation may produce adsorbed C and O atoms or combinations of these with H (as, for example, CH_x or OH). Surface carbon can participate in methane formation. The higher the H₂/CO ratio, the higher the probability of C hydrogenation, and the greater the availability of metallic sites able to undergo (hydrogen-assisted) CO dissociation. The second mechanism begins to play an appreciable role if the total amount of produced C atoms cannot be hydrogenated quickly enough, resulting in an accumulation of C and O on the surface. In the case of Co/MnO_x catalysts C and O coverages in excess of the monolayer capacity have been measured. Since there are no metallic sites for CO dissociation left on such a crowded surface, a different pathway via formates takes over. Such species have also been detected by DRIFTS. We consider CO insertion into surface hydroxyl to be responsible for the formation of formate which, upon hydrogenation, yields methane. Interestingly, the relative importance of the dual pathway mechanism of methane formation depends on the H₂/CO pressure ratio as well as on the choice of the support. For example, little evidence has been obtained for formate formation over Co/SiO₂ so far. The C and O surface coverages also remain below the monolayer limit in this case. The present contribution will develop the kinetic features of early and late methane formation and demonstrate the influence of various supports including, MnO_x, SiO₂ and TiO₂.

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The Consortium for Operando and Advanced Catalyst Characterization via Electronic Spectroscopy and Structure (Co-ACCESS) at SSRL

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The use of synchrotrons for in-situ and in-operando characterization of catalysts has proven to be essential for linking structural information to the performance of the working catalyst. The diverse techniques available at such user facilities, e.g. X-ray absorption spectroscopy, small- and wide-angle x-ray scattering, and x-ray microscopy provide crucial information that cannot be obtained by other means. At Stanford Synchrotron Radiation Lightsource (SSRL) at SLAC National Accelerator Laboratory we have initiated a new methodology, the Consortium for Operando and Advanced Catalyst Characterization via Electronic Spectroscopy and Structure (Co-ACCESS). The goal of Co-ACCESS is to enable any catalysis researcher (whether they study heterogeneous, homogeneous, electro- or photo-catalysis) with an interest in using X-ray methods for in-situ/in-operando catalyst characterization, to be able to pursue those interests in an expedient manner, with minimal barrier to conducting the research. This program builds on the proven success of the Synchrotron Catalysis Consortium at NSLS.

We are creating a holistic suite of integrated in-situ and operando synchrotron-based catalytic reactors by: (i) fabricating a suite of user-accessible in-situ cells, (ii) constructing automated feed delivery systems, (iii) coupled with on-line analytics. These experimental facilities are enhanced by investments and developments at SSRL, e.g. in data collection methods, and new beamlines, coupled with access to a wet chemistry laboratory, designed for catalysis studies, to allow the synthesis, proper handling, and activation of catalysts on-site. All of these activities are assisted by experienced staff.

This poster will focus on the capability development, with details provided on the infrastructure that is now available at SSRL for catalysis studies and a look forward to some of the new capabilities under development. These capabilities will be illustrated by research that have been collaboratively conducted: (i) The development of safe and routine operations at high pressure, facilitating research in syngas chemistry for higher alcohol synthesis and Fisher-Tropsch catalysis [1]. (ii) The application of high-energy resolution fluorescence detection methods for determining the active site complex [2][3], (iii) The development of time-resolved studies via continuous scanning of the monochromator, and (iv) The use of multi-modal methods, including XRD/XAS and XAS/TXM in order to extract more information for a given system [3].

SSRL offers a growing suite of techniques and methodologies for *in-situ/operando* advanced catalyst characterization. These techniques are driving new catalyst discoveries by determining the structure responsible for the activity, and vice-versa, the need to understand catalyst activity is also driving new experiments at SSRL

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Investigation of the α -Fe₂O₃ (0001) Surface via DFT Implemented with an Atom-Centered Basis

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Iron surfaces maintain the capability to exist in many different oxidation states which allows for utilization in profitable processes, often acting as a support for catalytic applications. Hematite (α -Fe₂O₃) is the most common naturally occurring form of an iron oxide and its (0001) surface has been shown to be most favorable under natural conditions [1,2]. The reduction of this surface can be altered by the presence of dopants due to their effect on the energetic and electronic properties of the surface. Understanding the reduction process of the α -Fe₂O₃ (0001) surface is necessary for its optimization within practical applications, but theoretical studies are often hindered by large atomic relaxations, unusual hybridization of wave functions and difficulty in handling localized electrons [3].

Prior density functional theory (DFT) studies only utilize plane wave calculations for surface optimizations due to their superior computational efficiency [4]. This work employs DFT implemented using an atom centered basis within the Crystal17 software package to benchmark the differences between said calculations and the results from Hensley et al. [5] where electrons were treated as projector-augmented waves. It is hypothesized that the use of this more chemically intuitive basis will provide superior correlation with experimental results in comparison to calculations performed using the more commonly use plane wave basis. Both the B3LYP and HSE06 functionals were utilized to investigate various α -Fe₂O₃ (0001) surface terminations, oxygen vacancies and the effect of dopants on oxygen vacancy formation to allow for comparison to plane wave calculation techniques.

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Enhancing the performance of partial oxidation of gasoline over Ni catalysts with Mo addition for SOFCs application

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Supported nickel catalysts are widely used in hydrocarbon reforming for hydrogen production. However, coke formation often leads to the rapid deactivation of Ni-based catalysts. In this work, we introduced Mo into Ni catalysts for isooctane (model gasoline) partial oxidation reactions. The Ni-Mo catalyst showed high reforming activity and stability with isooctane conversion of 97% and H₂ yield of 73% over 24 hours. Under the same reforming condition, the monometallic Ni catalyst without Mo showed a rapid deactivation due to coking. Our results showed a bigger average Ni crystallite size for the monometallic Ni catalyst compared to that of Ni-Mo catalyst following the partial oxidation reaction, which indicates that the higher degree of sintering took place for the sample without Mo. XRD results confirmed that Mo incorporated into the Ni lattice (by partial substitution of Ni atoms by larger Mo atoms) forming a Ni-Mo solid solution. Beside the Ni-Mo solid solution sites, Raman results also suggested that presence of well dispersed Mo=O species over Ni surfaces can be a possible active sites that are related to the coke resistance and stability of Ni-Mo/YSZ catalyst sample. The DFT-based calculation showed that Ni-Mo catalysts enhanced carbon-tolerance by increasing activation barriers of C-H cleavage and C-C coupling in the presence of Mo as compared with Ni/YSZ system. The DFT calculations further indicated that in the presence of Mo, the diffusion of carbon species is harder for Ni-Mo/YSZ system to form C-C bond and to grow into the coking. Ni-Mo catalyst was used as an internal micro-reforming layer on top of conventional Ni-YSZ anode supported single cells (Figure A). The single cell without the catalyst layer showed an unstable voltage and the overall cell performance exhibited a rapid degradation rate of 49 mV/h after 6 h of operation. By applying the Ni-Mo/YSZ catalytic internal reforming layer, the single cell displayed significantly improved stability with a low degradation rate.

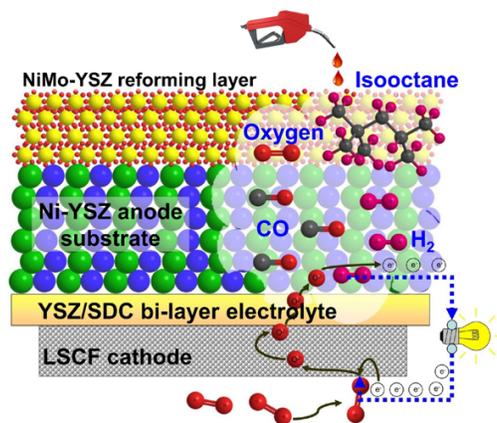


Figure A. Schematic of button-typed SOFC with a micro-internal reforming layer under the direct isooctane/air feed condition at 750 °C.

Multi-scale Models of Oxygen on Iron-Based Hydrodeoxygenation Catalysts: Elucidating the Effect of Promoters and Electric Fields

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Iron catalysts are highly selective for bio-oil hydrodeoxygenation (HDO) but quickly deactivate due to oxidation. It has been shown that precious metal-promoted, bimetallic, Fe catalysts not only limit oxidation, creating a longer-lasting catalyst, but also improve conversion and yield of aromatic hydrocarbon products.[1] This synergy is promising, but precious metals increase catalyst cost and complexity. To lower biofuel production cost, it is critical that more earth-abundant metals be utilized and that any precious metals are used precisely and judiciously. One way of reducing precious metal use is through the application of electric fields [3,4], which have demonstrated favorable effects on catalytic processes such as methane steam reforming.[2]

Here, we use density functional theory to determine how oxygen interacts with precious metal promoters in Fe-based catalysts. From this atomistic data, we constructed models of single catalytic Fe grains, capturing the multi-faceted morphology of a realistic catalyst surface (Figure 1a.i). These models indicate that Rh and Pd promoters weaken O adsorption, reducing O surface coverage over the Fe grain (Figure 1a.ii). Additionally,

positive electric fields destabilize surface-bound O by increasing repulsive O-O interactions [4], reducing O coverage by up to 7%.[3] By taking into account lateral interactions between Fe and the precious metal, we reveal dispersion trends which we expect to be predictive of the promoter's catalytic behavior. For instance, the most attractive Pd clusters are tightly packed, while the most repulsive Rh clusters are tightly packed. This is significant because attractive interactions are expected to form clusters, while repulsive interactions are expected to result in promoter dispersion, protecting more of the surface. These results align closely with the experimental results highlighting the superior performance of Rh over Pd, the latter of which is experimentally shown to form patches over the surface.[1] This work provides the fundamental insight needed to elucidate the precious metal role in bio-oil HDO, advancing efforts in developing cheaper and higher performing catalysts for the refinement of bio-oil to usable biofuel.

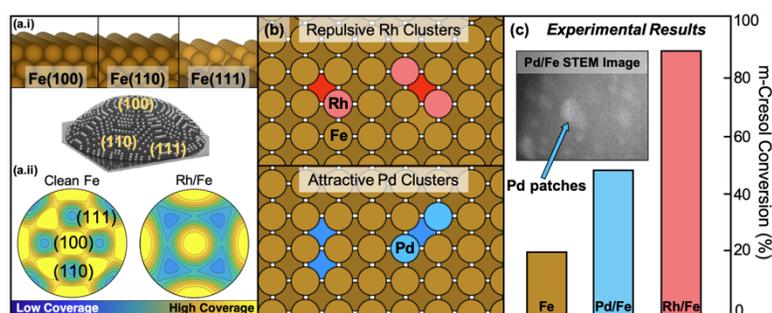


Figure 1: Elucidating the precious metal role in promoting HDO over Fe-based catalysts.(a.i) Fe facets used to construct a multi-faceted Fe grain.(a.ii) Top-down view of equilibrium O coverage over a multifaceted Fe grain.(b) The two most repulsive and attractive Rh and Pd clusters, respectively.

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Switchable Surfactants for the Preparation of Surface-Clean, Sinter-Resistant Supported Nanoparticle Catalysts and the Impacts of Calcination

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Established methods of preparing supported nanoparticle catalysts do not provide sufficient control over nanoparticle morphology. Classical methods typically require organic surfactants to passivate the nanoparticle surface to limit undesired size changes. Stabilizing ligands bound to the nanoparticle surface compete with reagents for active sites and typically significantly hinder catalytic activity. Commonly used methods of ligand removal such as calcination have detrimental effects on catalyst properties as exposure to high temperatures often results in significantly increased nanoparticle size and, thus, decreased total surface area for catalysis.

Here, we demonstrate a novel method for synthesizing highly active, monodisperse, supported nanoparticles using a switchable surfactant (SwiS) system. Using this method, nanoparticle size is finely controlled throughout synthesis and deposition. We show with X-ray photoelectron spectroscopy that supported nanoparticles prepared with SwiS are completely surface-clean after deposition, eliminating the need for any traditional activation steps such as calcination. Additionally, it is demonstrated that even a low-temperature calcination of surface-clean supported nanoparticles has detrimental effects on nanoparticle size, dispersion, catalytic activity, and surface chemistry. Supported nanoparticles prepared with SwiS are up to 700% more active in the hydrogenation of 4-nitrophenol than their calcined counterparts. Further, calcination results in the formation of an induction time in 4-nitrophenol reduction, reduces activation energy, and changes catalyst hydrophilicity demonstrating that calcination causes changes to catalyst properties beyond those associated with nanoparticle morphology. While calcination remains a widely used method catalyst activation, the negative effects of high temperatures on catalyst properties are often overlooked.

Comparative Analysis of Surface Configurations of CO Adsorbed on hcp and fcc Cobalt for the Fischer-Tropsch Synthesis

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The first step in Fischer-Tropsch (FT) synthesis over Co catalysts is carbon monoxide (CO) adsorption, which by and large out-competes dissociative hydrogen adsorption. Along with the fact that CO dissociation is not easy on the basal planes of Co catalysts, this fact implies that associatively adsorbed CO will likely have time to equilibrate with the imposed CO atmosphere and take on configurations relevant to the subsequent steps of the reaction. We present here a density functional theory (DFT) based investigation of these relevant configurations, taking into account the lateral interactions of CO through the construction of highly-predictive lattice gas models. Since both the face centered cubic (fcc) and hexagonal close packed (hcp) phases of Co have been shown to exhibit different FT activity, we compare these LG models and configurations as a function of the fcc and hcp phases; the primary difference being a large change in site-to-site distance (i.e. effectively different lattice strains).

By utilizing the Alloy Theoretic Automated Toolkit [1] to generate a large variety of extended Co(111) and Co(0001) surfaces with different coverages and configurations of CO, we construct a large library of CO/Co(111) and CO/Co(0001) structures. A LG model is fit to these data and subsequently optimized to produce the most predictive model possible for each system using our newly developed Ab-initio Mean-field Augmented Lattice Gas Modelling (AMALGM) code. The results reveal a non-trivial change in the first nearest neighbor (NN) interaction energy, reflected in a much more favorable full-coverage in the hcp surface (see Figure 1). However, we are able to show that the ground states of these two systems are largely unchanged despite this difference. Our results facilitate experimentally relevant comparisons of the two systems and indicate what kind of surface structures one should expect to be present in the early stages of FT synthesis given an hcp vs. fcc Co-based catalyst.

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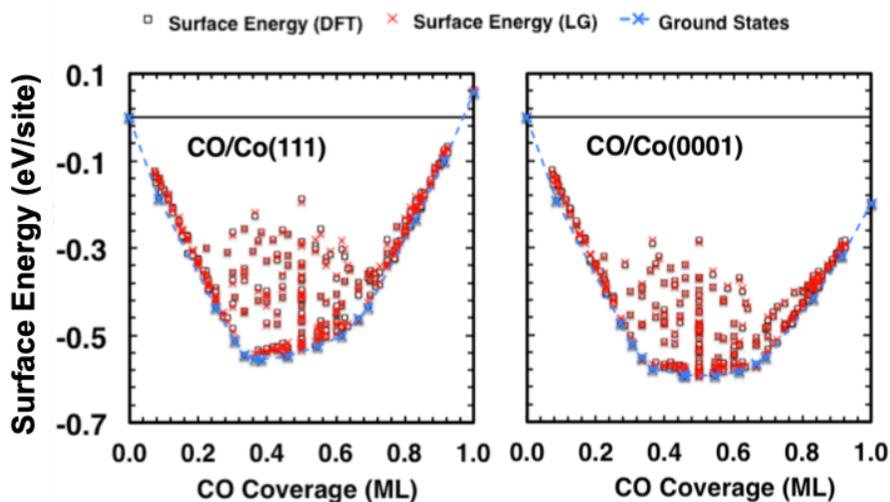


Figure 1. Surface energies (defined as $\theta \times E_{\text{ads}}$) and associated LG predicted energies for the fcc Co (left) and hcp Co (right) systems.

Small pore zeolite SSZ-13 supported Pd as highly stable low-temperature methane combustion catalysts

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The low-temperature catalytic methane combustion is an effective reaction for the removal of unburned methane from natural gas vehicle exhausts. This reaction is important for environment protection since methane displays 20 times higher greenhouse effect than CO₂. Palladium supported on Al₂O₃ is the most extensively studied catalyst for this application. However, Pd/Al₂O₃ suffers from severe deactivation in the presence of water vapor, an unavoidable component in engine exhausts. [1] Two mechanisms have been proposed for such a deactivation. One is the conversion of the catalytically active PdO phase to inactive Pd(OH)₂ by reaction with H₂O.[2] The other is the accumulation of hydroxyl groups on the support, which prohibits the transport of surface oxygen to the Pd surface.[3] In order to design catalysts with improved durability, utilizing hydrophobic supports to prevent accumulation of surface hydroxyl groups may be a viable solution. In the present study, we use zeolites as Pd supports since in this case, support hydrophobicity can be readily tuned by varying Si/Al ratios. Zeolites have been used as Pd supports in prior studies. However, those previous studies mainly focused on medium or large pore zeolites with thermal and hydrothermal stability too low for practical applications. [4, 5] Here we use SSZ-13, one of the most durable zeolite materials, as Pd supports.

In this work, a series of Pd supported on SSZ-13 with Si/Al ratio ranging from 6 to 36 were synthesized and tested for the methane combustion reaction. It is found that the Si/Al ratios have significant influence on the catalyst structures and performance. First, the Pd dispersion is greatly influenced by Si/Al ratio. At lower Si/Al ratios, Pd predominately stays as atomically dispersed Pd cations within the zeolite bulk; whereas at high Si/Al ratios Pd largely stays as external surface PdO nanoparticles. Secondly, the catalytic activity is also dependent on the Si/Al ratio. The methane combustion rates increase by orders of magnitude when support Si/Al ratio changes from low (6) to high (36). Third, and most importantly, the Pd/SSZ-13 catalysts with high support Si/Al ratios show durability much improved than Pd/Al₂O₃ under wet methane combustion conditions. A 50-hour steady-state test demonstrates that Pd/SSZ-13 deactivates ~10 times slower than Pd/Al₂O₃. Detailed kinetics studies show that this improved catalyst stability is correlated to power-law dependence of H₂O partial pressure during reaction, where Pd/SSZ-13 catalysts with higher Si/Al ratios display a ~0 order on H₂O partial pressure while Pd/Al₂O₃ exhibits a ~-1 H₂O partial pressure order. In summary, Pd/SSZ-13 with high Si/Al ratios show both higher activity and longer durability for methane combustion reaction. These correlate strongly to support hydrophobicity.

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Surface Reduction through Pt/Cu₂O Interfaces: A Combined Ambient Pressure, UHV, and DFT Study

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Recent catalysis research has been focused on converting CO₂ into useful chemical feedstocks due to its widespread availability in our current fossil-fuel-based economy [1]. Methanol, a valuable feedstock in many chemical processes, can be produced in this spirit using a CO₂ and H₂ stream in lieu of the traditional synthesis gas feed. This CO₂-based synthesis has been successfully catalyzed by copper supported on various mixed-metal-oxides, where interfacial metal-oxide regions have been identified as active sites for the reaction [2]. However, these catalysts are prone to poor cyclability as the reduction of CO₂ can facilitate oxide formation in these interfacial regions. Integration of precious metal dopants into these metal-oxide interfaces could improve their ability to dissociate gaseous H₂, allowing them to more easily maintain a sufficiently reduced state necessary for successful conversion of CO₂ to methanol.

In this work, we investigated the dissociation of H₂ and subsequent oxide reduction at Cu/Cu₂O interfaces doped with Pt atoms through a combination of ambient pressure, ultra-high vacuum (UHV), and density functional theory (DFT) studies. Ambient pressure experiments demonstrated that Pt/Cu(111) single atom alloys (SAAs) oxidized with varying degrees of O₂ exposure could be reduced by H₂ with reasonable kinetics (hours), in contrast to oxidized pure Cu(111) where such reduction is very slow (days). DFT calculations predict O adsorption near alloyed Pt sites to be weaker, implying the existence of bare Pt/Cu(111) patches that allow for H₂ dissociation and spillover to facilitate reduction in Pt/Cu(111) SAAs initially oxidized through lesser degrees of O₂ exposure [3]. This is justified further through CO TPD results from UHV studies where a high-temperature CO desorption peak is detected, presumably from CO bound to available surface Pt. Pt/Cu(111) SAAs initially oxidized through greater degrees of O₂ exposure lack these clean patches, as indicated by ambient pressure X-ray photoelectron spectroscopy (XPS) experiments. As DFT predicts H₂ dissociation to be thermodynamically unfeasible over Pt atoms densely surrounded by oxide, the reduction proceeds initially on the oxide around alloyed Pt sites, as the Pt likely weakens oxide bonds through its weaker binding of oxygen. After sufficient oxide reduction near these alloyed Pt sites has occurred, the reduction then continues using spilled-over H₂ from dissociation over newly-available surface Pt atoms. The success of these noble-metal doped regions in facilitating surface reduction demonstrates promise in cyclability improvement when applied to catalysts for reactions where metal-oxide interfaces are critical for high activity.

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Formic Acid Decomposition Reaction Under Externally Applied Surface Electric Fields

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The thermodynamic effects of an electric field on chemical reactions were outlined by Bergmann, et al. in a 1963 paper that related the strength of the field (F) to the equilibrium constant (K):

$$\frac{\partial(\ln(K))}{\partial F} = \frac{\Delta m}{RT} \quad [1]$$

where R is the universal gas constant, T is the reaction temperature, and Δm is the change in the electric moment of the molecules over the course of the reaction:

$$\Delta m = \Delta\mu + F\Delta\alpha \quad [2]$$

here, μ is the dipole moment and α is the polarizability of the molecules [1]. Equations 1 and 2 have been extensively cited by researchers investigating the effects of electric fields on chemical reactions but, to our knowledge, no one has yet applied the equations rigorously to the analysis of a reactive chemical system in an electric field [2-4]. This is partly because most chemical reactions have many side reactions that are difficult to account for when applying Equations 1 and 2.

In the present work, we use the simpler chemistry of formic acid decomposition to directly estimate the surface electric fields generated over a nickel catalyst inserted into an electric circuit using Equations 1 and 2. Formic acid (HCOOH) decomposes via two pathways into CO and H₂O (dehydration) or CO₂ and H₂ (decarboxylation). The effects of a “pure” electric field (i.e. no plasma generation, Joule heating, or Faraday reactions) on the reactivity of formic acid were experimentally tested using a nickel foam catalyst with nickel microparticles. The thermodynamic models and reaction data agree that positive surface fields should favor dehydration of formic acid while negative surface fields should favor decarboxylation of formic acid. These data are an important first step towards understanding electric field assisted heterogeneous catalysis, which until now has been lacking in concrete experimental support and has relied mainly on theoretical predictions via density functional theory (DFT)-based computations.

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Micro/Mesoporous Au@SiO₂ Core-Shell Nanoparticles for Alkalinity-Independent Selective Benzyl Alcohol Oxidation

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Silica-encapsulated gold core-shell nanoparticles (Au@SiO₂) were synthesized via a bottom-up synthesis to catalyze the selective oxidation of benzyl alcohol. The pore size, morphology, and composition of Au@SiO₂ was evaluated using N₂ gas adsorption, transmission electron microscopy, and inductively-coupled plasma mass spectroscopy, respectively. The nanoparticles exhibit a pore distribution with a peak at 27 Å, a size which enhances selectivity via preferential transport of the desired product (i.e. benzaldehyde) relative to larger, undesired products (i.e. benzoic acid/benzyl benzoate).

GC-FID analysis revealed the addition of potassium carbonate during the catalytic oxidation of benzyl alcohol increased conversion from 58% to 75% while only decreasing selectivity from 98.5% to 97.7%. These results suggest that the pore size distribution within the inert silica shell of Au@SiO₂ physically inhibits the formation of undesired products to facilitate the selective oxidation of benzaldehyde despite a basic environment which would drastically reduce selectivity under typical conditions [1].

An activation energy study revealed an unusually low activation energy of 23 kJ/mol. Combined with overwhelmingly rate-limited Thiele moduli, the particles appear to have a depreciated activation energy as a result of a catalyst that is not only product selective, but mechanism selective. As such, these particles are a promising platform for determining the impact of functionalization from on mass transport and surface chemistry discretely.

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Investigating Catalytic Function with Operando NMR

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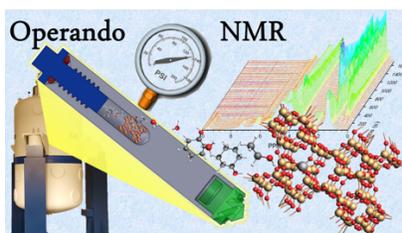
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Solid-state nuclear magnetic resonance spectroscopy (NMR) has served as an important tool for characterizing chemicals and catalysts by observing the chemical environments of the nucleus of interest. However, disparities between the spectroscopic environment and working conditions of the catalyst have challenged a firm understanding of the interactions between the catalyst surface and the chemical constituents within the system. Satisfying the conditions of high temperature and pressure often employed in catalytic applications are challenging when considering the sample is located inside a superconducting magnet and rotating several kilohertz to satisfy the magic angle spinning condition. These challenges have been addressed by the iterative development of high-temperature, high-pressure NMR rotors and sample treatment systems allowing for a carefully-controlled chemical environment to observed relevant interactions between the substrates and catalyst. The present design enables samples containing solids, liquids, and gases to be analyzed from -10 to 220°C, at pressures from vacuum to 100 bar, and at magnetic fields from 7 to 20 T. [1,2]

Employment of the developed NMR method to investigate catalytic systems reveals unique information on the bonding arrangements and reaction mechanisms under relevant conditions. Interactions of molecules such as light alcohols and water with catalytic surfaces (e.g. zeolite ZSM-5, silica, and silica-supported active centers) are probed in situ to reveal the bonding environments and evolution of the chemical species under working conditions. Both active site and substrate transformations are directly observable and provide insight into their interactions with each other. This approach enables the observation of the specific conditions required for a structural changes to the active site. [3] Indeed, operando MAS NMR offers an attractive method for revealing the nature of catalytic materials and their interactions with chemical species under working conditions.



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Generic Biphasic Catalytic Approach for Producing Renewable Diesel from Fatty Acids and Vegetable Oils

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According to the recent report issued by DOE/EIA¹, it is estimated that the diesel fuel consumption will increase by nearly 50% until 2040, which indicates the strong demand of diesel for transportation. The first-generation biofuels for diesel replacement, i.e. biodiesel, are synthesized through transesterification of vegetable oils or animal fats. However, biodiesel is a mixture of oxygenate compounds such as fatty acid esters, resulting in unfavorable cold flow properties, low energy density and poor storage stability^{2,3}. Such inferior properties might render biodiesel a less ideal choice in transportation fuels.⁴ For drop-in replacement, a complete deoxygenation of oils and fats via hydrogenolysis/hydrotreating seems to be a promising route since it produces renewable fuels in the form of pure hydrocarbons.

Conversion of fatty acids to diesel-range hydrocarbons suffers from elevated reaction temperature or low selectivity in single liquid-phase processes. Herein the biphasic interfacial catalytic process was developed for the decarboxylation of fatty acids to produce alkane hydrocarbons using Pd/C catalyst at the water-organic solvent interface. An exceptionally high carbon yield of $91.7 \pm 2.3\%$ (theoretical maximum 94.4%) and a high selectivity of $\sim 99\%$ to n-heptadecane were obtained from the conversion of stearic acid in the cycloalkane/water biphasic solvent system at a relatively low temperature (260 °C). The kinetic study of the conversion of stearic acid and oleic acid in the biphasic catalytic process was investigated and the activation barriers of both reactions were determined and compared to those of the monophasic catalytic processes. Both the experimental studies and MD simulations were performed to elucidate the synergistic effects of water and various organic solvents, which stabilize the carboxylate group and the hydrophobic hydrocarbon tail in a fatty acid molecule, respectively, and improve the kinetic rates and the selectivity. The application of the biphasic tandem catalytic process (biTCP) approach was further extended to the decarboxylation of a wide selection of saturated and unsaturated fatty acids, triglycerides (e.g., glyceryl trioleate), and oilseed biocrude oil (e.g., canola oil) to produce high-quality diesel fuels.

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First observation of super electrophilic metal (Pd^{+2}) cations in a zeolite (SSZ-13): new Pd chemistry for adsorption and catalysis applications

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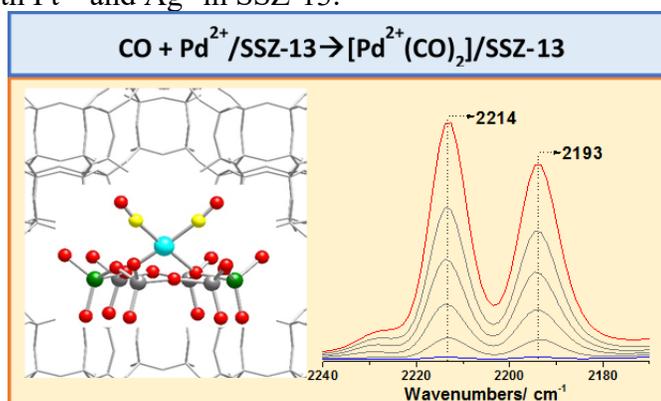
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The results of our combined experimental (FTIR, XPS, HAADF-STEM, XANES) and density functional theory study reveal that Pd ions in zeolites, previously identified as Pd^{+3} and Pd^{+4} ,¹⁻³ are in fact present as super electrophilic Pd^{+2} species (ion pairs with the negatively charged framework oxygens).^{4,5} This is the first observation of a super-electrophilic metal cation in a zeolite.

In this contribution we re-assign the spectroscopic signatures of these species, discuss the unusual coordination environment of “naked” (ligand-free) Pd^{+2} in SSZ-13, and their complexes with CO and NO. With CO, non-classical, highly positive $[\text{Pd}(\text{CO})_2]^{2+}$ ions are formed with the zeolite framework acting as a weakly coordinating anion (ion pairs). Non-classical carbonyl complexes also form with Pt^{+2} and Ag^{+} in SSZ-13.



The $\text{Pd}^{+2}(\text{CO})_2$ complex is remarkably stable in zeolite cages even in the presence of water, unlike its few known organometallic counterparts. Dicarbonyl and nitrosyl Pd^{+2} complexes, in turn, serve as precursors to the synthesis of previously inaccessible Pd^{+2} -carbonyl-olefin $[\text{Pd}(\text{CO})(\text{C}_2\text{H}_4)]$ and -nitrosyl-olefin $[\text{Pd}(\text{NO})(\text{C}_2\text{H}_4)]$ complexes. Overall, we provide novel insight into the interactions of (polyvalent) metals with the zeolite framework, and show the new chemistry of Pd/SSZ-13 system with implications for adsorption of CO, NO and ethylene molecules and catalysis (butadiene formation from ethylene).

First observation of super electrophilic metal (Pd⁺²) cations in a zeolite (SSZ-13): new Pd chemistry for adsorption and catalysis applications

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Tuning Ligand Characteristics to Enhance Activity of CH Transformations in Bio-inspired Dicopper Catalysts

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Our goal is to utilize computational tools to investigate the mechanisms of CH activation in bio-inspired dioxo-dicopper complexes. The conversion of alkanes into high-value compounds is a long-standing challenge due to the inert character of CH bonds. Several synthetic efforts have focused on duplicating the activity of the selective oxidation enzyme, particulate methane monooxygenase, [1] by dicopper complexes [2]. However, synthetic and computational studies are challenging owing to poor understanding of the active site and reaction mechanisms [3][4], possibility of spin crossover [5], and multi-reference character of the dicopper center.

We investigate methane hydroxylation with model dioxo-dicopper ($[\text{Cu}_2\text{O}_2]^{2+}$) complexes using density functional theory, energy decomposition analysis (EDA), and activation strain model. We demonstrate that single-step oxo-insertion is the preferred mechanism of CH activation based on both potential energy surfaces and the comparison of calculated and experimental Hammett relationships. EDA indicates that oxo-insertion transition states are stabilized by electron-withdrawing ligands via charge transfer interactions [6]. Based on these insights, we see the possibility to enhance catalytic activity by independently tuning various ligand characteristics. We subsequently deduce linear relationships between barriers and ligand characteristics, particularly bite angles of bidentate N-donors. EDA and strain analysis show that small bite angles with less methyl substitution at the N lower strain energy, and therefore, lower barriers. Going forward, we will focus on analyzing decomposed barrier components to understand how the catalytic activity relates to ligand descriptors like bite angles, Hammett parameters, Sterimol parameters, etc.

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Aldol Condensation of Acetone over Single-Facet Dominant Anatase TiO₂ (101) and (001) Catalysts

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The catalytic aldol condensation of aldehydes and ketones is an important reaction for C-C coupling and oxygen removal in the transformation of biomass-derived oxygenates into fuels and chemicals. TiO₂ containing Lewis acid-Brønsted base site pairs (Ti^{δ+}-O^{δ-} pairs) is widely studied as a catalyst for this reaction. In this work, two anatase TiO₂ nanocrystals, with preferential exposure of (101) and (001) facets, respectively (denoted as TiO₂ (101) and TiO₂ (001), respectively), were synthesized as model catalysts to gain mechanistic insight into elementary steps and the active site requirements for acetone condensation on TiO₂ facets, via the combination of kinetic, spectroscopic, and theoretical studies. The infrared spectroscopic studies confirmed the existence of abundant acetone molecules hydrogen-bonded to the surface OH groups on TiO₂, other than those adsorbed on Lewis acid site (Ti^{δ+}), during steady-state reaction. The kinetic measurements for acetone condensation were carried out upon co-feeding isopropanol as reaction spectator, which mitigated the catalyst deactivation by diluting the acetone coverage and thus suppressing the secondary aldol condensation reactions forming heavy products. We demonstrated that the inter-molecular C-C coupling is kinetically relevant step for acetone condensation on a spectator-populated TiO₂ surface. With the assistance of density functional theory (DFT) study, we proposed that the C-C coupling occurs between the enolate formed on Lewis acid site (Ti^{δ+}) and the acetone hydrogen bonded to surface OH group, as depicted in Figure 1a. Both the kinetic measurement (Fig. 1b) and the DFT calculation (Fig. 1a) indicated that TiO₂ (001) facet has lower apparent activation energy for acetone condensation, in comparison to (101) facet. The DFT calculation also indicated that the (001) facet has lower acid and basic strengths than (101) facet. Therefore, the higher activity for acetone condensation on TiO₂ (001) facet is likely a consequence of its smoother surface geometry than (101) facet, which has less hindrance for the inter-molecular C-C bond formation.

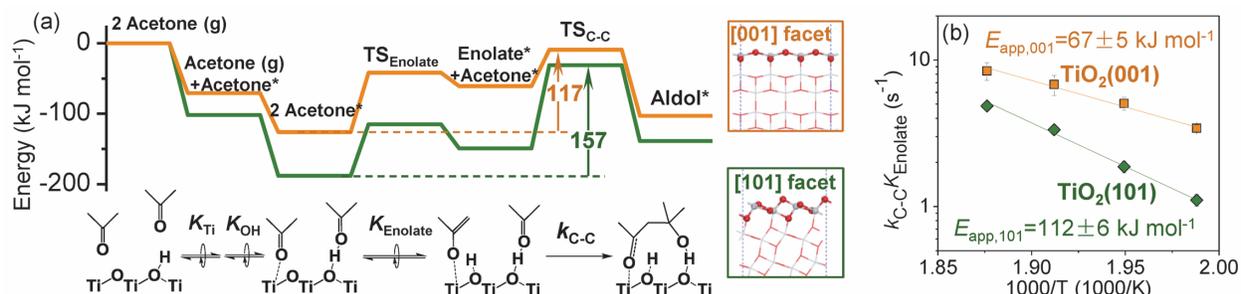


Figure 1. (a) Energy diagram of acetone condensation on (001) and (101) facets of anatase TiO₂ (DFT calculation); (b) Arrhenius plots of the measured effective rate constant ($k_{C-C}K_{Enolate}$) for acetone condensation on TiO₂ (001) and TiO₂ (101) catalysts

Strong Solid Bases for Biomass Conversion via Condensation

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The activity of strong bases has been investigated by means of several reactions to evidence their basic properties and the mechanism involved and demonstrate their great practical application of condensation reactions in Biomass upgrading.

Upgrading biomass relies on condensation reactions for building longer carbon chains, removing oxygen by dehydration and transformation of functional groups such as ketonization of carboxylic acids. With the aim to challenge the current application of homogenous catalysts for the condensation of bio-based ketones and esters, several strong basic catalysts based on magnesium oxide (MgO)¹⁻² and hydrotalcites (HT)³⁻⁵ have been developed and tested for aldol condensation of ketones and Claisen condensation of esters. The potassium and strontium doped HT resulted in good conversion and selectivity of hexaedione to methylcyclopentone, but less activity for 2-butanone conversation. The result of Claisen condensation of acetates and succinates disclosed the products of trans-esterification and decarboxylation that indicated the correlation of oxygen and water in the reaction. The comparison of catalyst basicity and the reaction mechanism will be discussed in detail.

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Hierarchically Porous M-N-C (M = Co and Fe) Single-Atom Electrocatalysts for Fuel Cells

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The integration of hydrogen into power generation applications is critical for an environmental friendly and sustainable energy pattern. Fuel cells are considered as one of the cleanest energy conversion technologies. The efficiency and cost of fuel cells, however, are still hurdled by the development of cost-effective catalysts that reduces oxygen at the cathode side. Currently, there is an intensive research efforts for highly efficient electrocatalysts based on low-cost and earth abundant elements. Improving non-precious metal catalysts require rational control over their size, shape, composition, and structure. In particular, single-atom catalysts (SACs) show great promise owing to their high catalytic activity, stability, selectivity, and 100 % atom utilization. Through innovative synthesis methods, we have developed a universal strategy to design and construct hierarchically porous SACs with highly active sites, MN₂ (M = Fe or Co), which outperform the commercial precious-metal catalysts and show great potential for practical proton-exchange membrane fuel cells. Combining advanced characterization techniques and theoretical simulation, we further unravel the origin of the high catalytic activity of SACs at atomic level. The findings shed light on the catalytic reaction mechanism of SACs and may help future development of low-cost and highly efficient fuel cell catalysts.

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Conversion of 2,3-Butanediol to 1-3 Butadiene over Indium Oxide Catalyst

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Butadiene (BD) is an essential precursor for the large-scale synthesis of polymers and rubbers, where the predominant method of butadiene production is through the steam cracking of petroleum feedstocks. However, due to increase in the demand and the interest in the renewable component of polymer production, catalytic dehydration of 2-3 butanediol (2-3 BDO) to 1-3 butadiene (1-3 BD) has been under great investigation, as 2-3 BDO can be produced via biomass fermentation with relatively low cost. Several studies have been done, with increasing interest in the use of rare earth oxides (REO) as the catalytic environment. In this work, indium oxide (In_2O_3) will be used in the two-step dehydration process of 2-3 BDO to Methyl Vinyl Carbinol (MCV) and finally to 1-3 BD. Concurrent measurements using XRD, XPS and TPD absorption of the catalyst will be used to describe and characterize the potential activity sites and how catalyst synthesis changes affects the overall conversion of 2-3 BDO to 1-3 BD.

Fundamentals of Multiphase Reaction Engineering for CO₂ Free Hydrogen Production from Natural Gas

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Hydrogen production is an essential component of the refining and petrochemical industries. Steam-methane reforming (SMR) is the primary method of hydrogen production in the U.S. Sorption enhanced steam-methane reforming (SE-SMR) is an attractive adaption of SMR that reduces operating temperature and down-stream processing[1]. The primary drawbacks of SE-SMR materials are incomplete carbonation, slow carbonation kinetics, loss in activity upon cycling, and high regeneration temperature[2].

Nanofibrous calcium oxide, synthesized via electrospinning, was compared against calcium oxide synthesized via calcium acetate decomposition, hydrothermal synthesis with the aid of a surfactant, and natural sources. A thermogravimetric analyzer found that the sorption capacity of calcium oxide from nanofibers to outperform other samples, reaching stoichiometric capacity 0.79 g_{CO₂}/g_{sorbent} after 1 hour at 600°C, 1 atm, and 100% CO₂. The capacity of calcium oxide nanofibers and CaO derived from natural sources were measured over repeated carbonation and calcination cycles. Both calcium oxide nanofibers and natural calcium oxide lost ~33% of their initial capacity after ten cycles [3]. To mitigate these capacity losses, various metal nitrates were added to the calcium nitrate electrospinning solution, at various compositional ratios, as dopants to increase the stability of the sorbent. The dopants studied comprised of metals from Groups 2, 3, 4, 12, and 13 on the periodic table of elements. These doped-sorbents were shown to have various positive and negative effects on capacity and stability. Generally, sorption capacity increased with the Tammann temperature of the additive metal, the most stable additives had a 3⁺ oxidation state, and various additive metals reacted with CO₂ to increase the sorption capacity compared to non-carbonating additives. Doped and undoped samples were characterized with SEM, BET, XRD, and TEM to identify the properties that influence capacity, kinetics, and stability.

SE-SMR studies verified that the samples with higher capacity indeed had longer breakthrough times, with calcium oxide nanofibers having the longest breakthrough time. After 10 cycles additive modified calcium oxide outperformed the pure calcium oxide nanofibers due to loss of sorption capacity [3]. Reactor studies were carried out to determine the transport effect on breakthrough time. In these studies, the of calcium oxide sorbent and nickel catalysts were varied from nanometer scale, using a single material, to millimeter scale, using catalyst pellets and sorbent pellets. The experimental results are complimented modeling the behavior based on the material sorption kinetics and capacity.

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An in situ formed metastable active site catalyzes the formation of the carboxyl intermediate during the water-gas shift reaction

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Definitive experimental proof for catalytic pathways and active sites during the low-temperature water-gas shift reaction remains elusive. Herein, we combine spectroscopic, kinetic, and computational analyses to address the decades-long mechanistic controversy by studying the reverse water-gas shift over Pd/Al₂O₃. Isotopic transient kinetic analysis clearly established the minor role of the formate (HCOO) intermediate. Moreover, hydrogen titration experiments unambiguously confirmed the intermediacy of carboxyl (COOH) for the first time. The ability to decouple the parallel formate and carboxyl pathways led to the identification of a distinct active site exhibiting regio- and chemoselective H-addition to CO₂ to yield carboxyl. The metastable active site is formed in situ, resulting in hydroxylation of the metal-support interface and electronic restructuring of Pd via reduced coordination. Parallel atomistic simulations of the active site electronic structure and mechanistic landscape provided a framework consistent with experimental observations. Our study highlights the dynamic creation of a coordinatively unsaturated metal site caused by substrate adsorption on an adjacent support site.

SCR Activity enhancement of Cu-SSZ-13 through adding a secondary oxide

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Cu-SSZ-13 is currently considered as state-of-the-art for eliminating NO_x emissions from transportation sources via NH₃-SCR (selective catalytic reduction using NH₃ as a reducing agent), owing to superior activity and durability versus its predecessors (*e.g.*, MFI- and BEA-based SCR catalysts). [1] However, criteria emission (*i.e.*, NO_x) legislation combined with the pursuit of improved combustion efficiency dictate that low temperature activity for NO_x reduction must be improved while high temperature selectivity must remain high in durable fashion. In the presence of NH₃, the transformation of surface adsorbed NO species forming a reactive NO₂-like intermediate was demonstrated as the rate determining step for the reduction of NO at low temperature. [2] One approach to improve performance is through the inclusion of a secondary oxidative promoter that, when coupled with the parent SCR catalyst, is able to facilitate this rate limiting step. Such an approach has additional associated benefits, including low-temperature reduction of NO_x by the secondary oxide promoter directly, and shifting to an oxidative realm at higher temperature to reduce fast SCR dependence on incoming NO₂.

In this presentation, a series of ZrO₂-based transition metal oxide materials were prepared and used as the oxidative promoter of Cu-SSZ-13 SCR catalyst. Proper integration of the secondary oxide with Cu-SSZ-13 facilitates improved low-temperature activity while retaining superior high-temperature selectivity. XRD and EPR were used for characterization of the active species, and to shed light on the pathway of secondary oxide impact on the parent Cu-SSZ-13, which will be discussed in detail. Secondary oxide phase chemistry and the pathway of integration with Cu-SSZ-13 will also be discussed as it relates to key parameters of the system.

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Methyl formate hydrogenation to higher hydrocarbons over Mn- and Ti-oxide promoted cobalt catalysts

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Methyl formate has been considered since the early 1990s as a potential platform molecule for C1 chemistry [1]. The fact that this molecule contains CO and H₂ in a 1:1 ratio makes it a potentially suitable feedstock for the preparation of hydrocarbon chains. Recently, we have established that it is possible to produce chain-lengthened paraffins from methyl formate via a Fischer-Tropsch akin process utilizing cobalt-based catalysts at atmospheric pressure. With further exploration, methyl formate hydrogenation may also provide a novel route for the synthesis of olefins and oxygen-functionalized hydrocarbons. This work will provide kinetic and mechanistic insight into the atmospheric pressure hydrogenation of methyl formate over cobalt catalysts promoted by Mn- and Ti-oxides using transient response methods. Manganese and titanium were selected due to their documented promoter effects for cobalt-based catalysts studied under conventional Fischer-Tropsch synthesis conditions [2, 3].

Chemical Transient Kinetics (CTK), as applied in the present studies, relies upon the abrupt switching between a non-reactive (H₂ + Ar) and a reactive gas mixture (H₂ + He + methyl formate) while maintaining constant molecular flow conditions at the inlet to a catalyst bed. The initial construction of the catalytically active surface, termed the “build-up”, occurs when reactants are admitted to the gas phase over a freshly reduced catalyst surface. Likewise, the removal of reactants from the gas phase results in a “scavenging” of the surface as residual adsorbed species are hydrogenated and desorb. Observation of the build-up and scavenging behaviors for a catalytic system provides mechanistic insight unattainable from a steady-state kinetic analysis.

During the build-up of the methyl formate hydrogenation reaction over a Co-MnO_x catalyst at atmospheric pressure and 220 °C, alkanes are observed to form in the sequence of their carbon numbers. Apart from methane, which is the first product observed, chain-lengthened alkanes appear once methyl formate decomposes to yield CO in the gas phase. The time-correlation of chain lengthening initiation and CO appearance in the gas phase places a strong argument in favor of a CO insertion mechanism being in operation. Differing from earlier studies on methyl formate hydrogenation in our lab, in which only alkanes were observed over Co/MgO catalysts [4], we also observe olefins. Methanol production is also observed, time-delayed relative to the appearance of gaseous CO.

We hypothesize that formyl groups (resulting from the dissociation of methyl formate) adsorbed on the catalyst surface undergo decarbonylation to yield CO, which subsequently inserts into the bonds of surface alkoxy or hydroxyl groups. The resulting carboxylate-type species may then be hydrogenated to produce alkanes/alkenes or turned into a (C+1)-alkoxy homologue subject to another CO insertion, and therefore, chain lengthening. Such a scenario would also be able to account for the formation of oxygenated products.

Methyl formate hydrogenation to higher hydrocarbons over Mn- and Ti-oxide promoted cobalt catalysts

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Influence of substrate complexity on the enthalpy-entropy compensation for rate enhancement in molecular sized confinements

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Enhancing the acid catalyzed dehydration of alcohols is key to many organic synthetic transformations. The dehydration of alcohols in the aqueous phase is catalyzed by hydrated hydronium ions, provided either by homogenous or solid acids. The enthalpy and entropy of activation for organic transformation inside zeolite pores is heavily influenced by the local structure and interaction of reactants with the zeolite pores and hydronium ions along with the stabilization of reactant intermediates along the reaction pathway. In this work, we contrast the fundamental kinetic parameters for dehydration of heptanols from phosphoric acid to the parameters obtained from molecular sized confinements, specifically, narrow pore HMF1 and wider pore HBEA.

Enthalpy of activation ($\Delta H^{0\dagger}$) and free energy of activation ($\Delta G^{0\dagger}$) for alcohol dehydration in homogenous acids follow the stability of carbenium ion following C-O bond cleavage in an E1 mechanism (Figure 1 below). Increased contact for transition state (TS) relative to the ground state with internal zeolite pores leads to lower $\Delta H^{0\dagger}$ and $\Delta S^{0\dagger}$ for HMF1. Overcompensation of $\Delta H^{0\dagger}$ in 2-methyl-2-hexanol in HBEA as compared to HMF1 makes the reactivity to be higher on HBEA than HMF1. TS for a highly branched 3-ethyl-3-pentanol is disordered, leading to high $\Delta H^{0\dagger}$ and $\Delta S^{0\dagger}$ on HBEA while leading to diffusion limitations in HMF1.

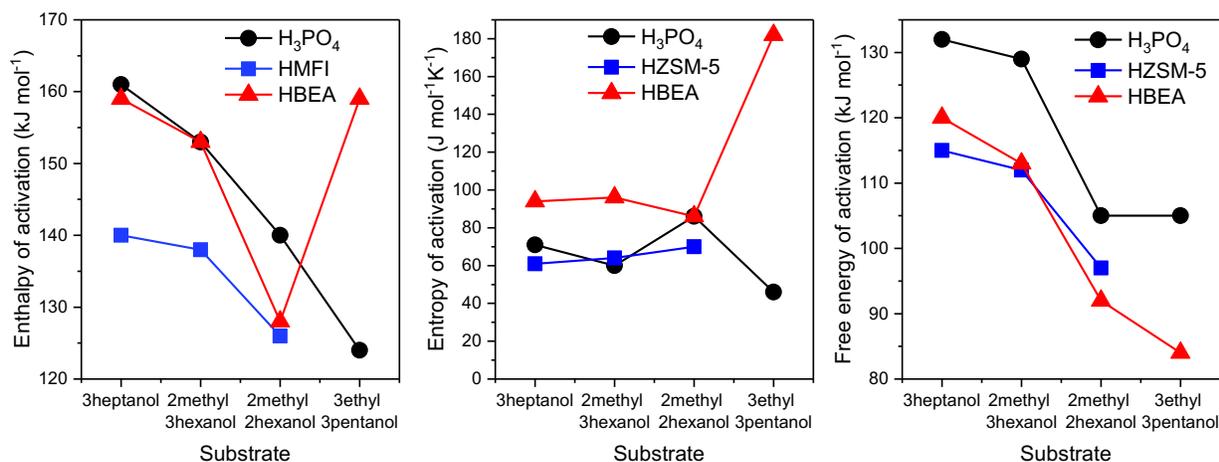


Figure 1: Enthalpy, entropy and free energy of activation for studied heptanols. Concentration: 0.25 M solution in water.

Identifying active-site ensembles at the atomic scale

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The identification of active-site ensembles is a well-known endeavor in heterogeneous catalysis. To efficiently determine active-site motifs present under reaction conditions within the vast design space of bimetallic nanoparticles (NPs), we need to derive density functional theory-based predictive models. We have recently addressed this need through a new class of energy correlations that forge robust connections between the structure of active sites, their thermodynamic stability, and the energy space of reaction intermediates.[1-4] Our models rely on a limited set of parameters derived from simple slab calculations, but are nonetheless directly transferable to NPs spanning a broad structure and composition space. In the present contribution, we demonstrate the significance of our models by identifying active-site ensembles that catalyze propene combustion on PtPd nanoalloys [5].

Kinetic studies of propene combustion reveal that both co-feeding water as well as increasing the nanoparticle size (from 2 to 10 nm) increases the TOF of this reaction. These observations lead us to hypothesize that OH* formed from dissociated water causes the PtPd nanoalloy to reconstruct during the reaction, exposing a greater fraction of active-site motifs on larger nanoparticles. We test this hypothesis by using our models to rapidly determine the impact of OH* adsorption on the surface energies of different surface terminations. We find that OH* preferentially stabilizes surfaces possessing undercoordinated sites (e.g. (211) and (110) surfaces) over terraces (e.g. (111) and (100) surfaces). The corresponding Wulff constructions reveal that the highly faceted nanoparticles, exposing mainly (111) and (100) terraces, reconstruct under reaction conditions into spherically-shaped particles exposing (211) and (110) surfaces. By counting the density of candidate active-site ensembles across a library of such Wulff-constructed PtPd nanoparticles having different sizes, we find a 1:1 correlation of the density of 7-7 coordinated bridge sites with the experimentally measured TOFs. Since these undercoordinated sites also have lower C=C scission barriers in comparison with terraces, we conclude that dynamically formed step sites are active for breaking C=C bonds in propene combustion.

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Ethanol Conversion to C5+ Alcohols for Diesel Fuel Blend Stocks

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Recent breakthrough in biomass conversion technology will progress to produce surplus ethanol beyond the 15% gasoline blending requirements in the near future. Excess ethanol can be used as platform molecule for synthesizing valuable chemicals, fuel precursors and fuel blend stocks. In this work, first ethanol is converted to C5+ ketones through thermochemical pathway over Pd promoted ZnO-ZrO₂ based mixed oxide catalyst. In this chemistry, ethanol goes through sequence of complex reaction steps to generate the C5+ ketones. Maintaining synergistic effect between the multifunctional catalytic systems and optimum reaction conditions is important to generate C5+ ketones at high yield while avoiding the undesired by product formation. Suite of catalyst characterization is utilized to identify the nature of catalyst active sites and to improvise the catalytic performance. The C5+ ketones are then hydrogenated to corresponding alcohols over a commercial hydrogenation catalyst. Finally, C5+ alcohols is analyzed for fuel properties such as cetane number, flash point, viscosity, freeze point and boiling point to measure against the suitability as a diesel fuel blend stock.

Engineering Advanced Transition-Metal Based Electrocatalysts for Oxygen Evolution Reaction

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The ever-increasing energy demands and growing environmental awareness have stimulated extensive research on the development of alternative energy conversion and storage technologies. Electrochemical water splitting is among the most appealing technology that receives more and more attention. However, the kinetically sluggish oxygen evolution reaction (OER) greatly hurdles its wide application. To make the water splitting process more energy-efficient and economical, developing high-performance noble metal-free catalysts has aroused great attention due to their distinct advantages, such as relatively low cost and toxicity, great flexibility in terms of structure and morphology, and satisfying electrochemical performance. We focus on the rational design of porous nanostructures with tunable composition and defect engineering, aiming at increasing the density and the reactivity of the active sites. With optimized structural and compositional parameters, our nanostructured electrocatalyst exhibited excellent OER activity and stability, holding great promise in water splitting. In particular, our highly disordered nickel and iron based OER catalyst have shown promising performance in alkaline exchange membrane (AEM)-based electrolysis.

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Developing Stability Criteria of Isolated Metal Adatoms on a Well-Defined Copper Oxide Film

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Single-site catalysts (SSC) are attractive materials due their high selectivity and atomic efficiency [1]. In the case of SSC's consisting of supported metal adatoms, strong interactions between the metal species and the support are required to anchor the adatom on the surface. Oxides are found to be effective supports for metal adatoms, preventing their agglomeration and thus promoting the catalyst's thermal stability [2,3]. Despite this, adatoms can still diffuse into the bulk, causing the catalyst to deactivate. STM measurements of a thin surface oxide film, specifically the "29" Cu_xO/Cu(111) surface oxide, with atomically dispersed Pt after CO oxidation, found that some Pt adatoms previously planted on its surface were missing, suggesting that Pt was able to go subsurface after the reaction [2]. This brings us to the investigation of the segregation tendencies of various metal adatoms on a thin-film copper oxide surface, using a model "29" Cu_xO/Cu(111) surface oxide as an example.

In this work, we determine the segregation tendencies of Ag, Au, Pd, Pt and Rh adatoms on a pristine "29" Cu_xO/Cu(111) surface from first principles using density functional theory based calculations (schematics in Figure 1). To deconvolute the properties which govern the segregation of the metal (M) adatom from the surface, we first correlate the adatom segregation energy (Figure 1) to the formation energy of a bulk Cu₃M alloy, the bulk metal surface energy, and the strain energy induced from fitting the metal adatom into a fixed Cu lattice. We also perform a differential charge analysis and oxygen binding energy calculations to determine how oxygen adatoms affect the segregation tendencies on the surface of an oxide film. The oxide film's influence is further isolated through a comparison of the segregation energy trends on a Cu surface in the presence and in the absence of a surface oxide. We find that metals with surface energies that are lower than that of Cu result in favorable adatom segregation energetics. The ability of a metal adatom to segregate from Cu increases in the following order: Rh, Pt, Pd, Au, and Ag, where Ag is the least likely to diffuse into the bulk. A density of states (DOS) analysis confirms that segregation is favorable for metal adatoms with d-band centers that are further away from the Fermi level than Cu. A more segregated adatom also binds weaker to CO. We thus propose the difference between the surface energy of the bulk adatom metal and that of Cu as a descriptor for its segregation tendency on the "29" Cu_xO/Cu(111) surface. Using this information, we can now predict stable adatoms to be supported on "29" Cu_xO/Cu(111) before investing into more computationally expensive calculations.

Developing Stability Criteria of Isolated Metal Adatoms on a Well-Defined Copper Oxide Film

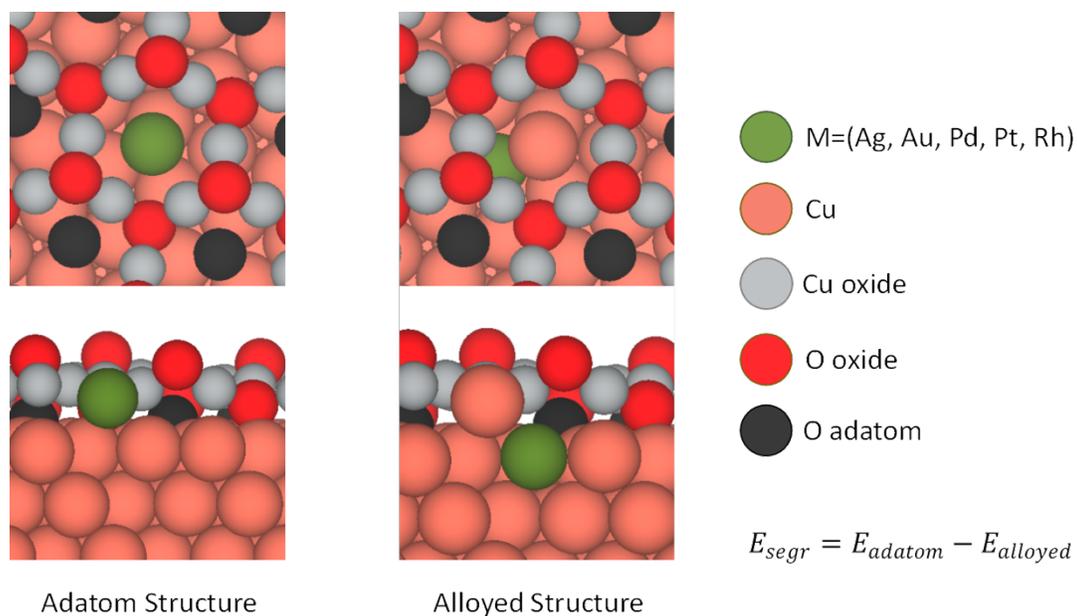


Figure 1: Schematic of the adatom and alloyed structures used to calculate segregation energies

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Effects of Alkali and Alkaline Earth Co-cation Additives to Cu/SSZ-13 SCR Catalysts

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The commercialization of hydrothermally robust small pore copper exchanged Cu/SSZ-13, as selective catalytic reduction (SCR) catalyst for diesel engine exhaust aftertreatment, has been a major milestone in environmental catalysis in recent years[1, 2]. Despite its great success, there is still need, and room, to further improve its performance, particularly in low-temperature activity, high-temperature selectivity, and long-term durability. Recently, it has been discovered that certain cationic additives (Na^+ , Ce^{3+} , etc.) can be used to fine tune catalytic performance of this catalyst [3-5]. These additives play three roles: (1) competing with Cu-ions for catalytic exchange sites; (2) neutralizing Brønsted acid sites thus preventing dealumination during hydrothermal aging; (3) providing NH_3 adsorption function as Lewis acids. These roles have not yet been thoroughly investigated. In this work, a series of Cu/SSZ-13 catalysts with and without Na^+ (K^+ , Ca^{2+}) co-cations have been prepared and systematically investigated by means of kinetics, chemical titrations, spectroscopies (EPR and NMR), and theoretical calculations with DFT.

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Synthesis and Characterization of Cu@Pd Core-Shell Structured Nanoparticles for the Interconversion between CO₂ and Formic Acid

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The worldwide reliance on fossil energy produces an enormous amount of carbon dioxide (CO₂) emission [1]. The global climate change caused by the large CO₂ concentration in the atmosphere increases the frequency of drought and catastrophic storms that further impact our crop yields. One way to minimize the CO₂ concentration is via a regenerative energy system that converts CO₂ into formic acid during the “charging phase” and produces electricity by formic acid oxidation during the “discharging phase”. Currently, Palladium (Pd) is one of the most efficient electrocatalysts for the interconversion between CO₂ and formic acid, but it is very expensive and its surface is susceptible to CO poisoning. Therefore, there is a critical need to improve electrocatalytic performance and reduce the material cost of Pd for this sustainable technology to be viable. One strategy to achieve the objectives is to produce core@shell nanoparticles and utilize the electronic interaction between the metal cores and Pd shells at the bimetallic interface to decrease the bonding strength of key intermediate species on the Pd surface improving its electrocatalytic activity and long-term stability. In this work, Cu@Pd nanoparticles were synthesized via the adsorbate-induced surface segregation method. Synthesized samples of nanoparticles in this work were characterized by cyclic voltammetry (CV) and controlled potential electrolysis (CPE). CV data suggest that the transfer of charges from the Pd shell to the Cu core decreases the bonding strength of key intermediate species on the surface of Pd. This electronic perturbation of the catalyst surface lowers the energy barrier for CO₂ hydrogenation into formic acid and make the formation of CO on the surface of Pd less favorable. The CV shows that the CO₂ reduction current density is 0.21 mA/cm² at -0.15 V vs RHE and the formic acid oxidation current density is 5.65 mA/cm² at 0.37 V vs RHE on the surface of Cu@Pd, which is about 6.2 times and 7.9 times higher than the current density on commercial Pd, respectively. The CPE data shows the long-term stability of the Cu@Pd catalyst is higher than commercial Pd when the catalyst is used for CO₂ reduction and formic acid oxidation.

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Single-Step Conversion of Ethanol to Butadiene and Butenes over Ag/ZrO₂/SBA-16 Catalysts

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Ethanol is an attractive biomass-derived feedstock for the production of fuels and industrially relevant product since it is presently produced at commercial scale from renewable biomass and waste sources. A flexible catalytic process was developed for the single-step conversion of ethanol to either butadiene or n-butene-rich olefins over Ag/ZrO₂/SiO₂ catalysts. Butadiene is a highly desired compound used in the production of tires and other essential synthetic polymers and elastomers. N-butene-rich olefins are valuable as fuel precursors. Although the single-step ethanol to butadiene reaction has traditionally exhibited lower yields—where higher selectivities to butadiene (i.e. 70%) are only achievable at lower conversions (i.e. 40%)—we recently reported a study on the Ag/ZrO₂/SiO₂ system finding an optimal composition using SBA-16 support resulting in an outstanding performance of 99% conversion of ethanol at 71% selectivity to butadiene under mild process conditions (325°C, 1 atm, 0.23 h⁻¹ under N₂) [1]. Over the same catalyst, operating under a reducing environment (under H₂) leads mainly to the formation of n-butene-rich olefins with yields reaching ~85%. Computational atomistic modeling coupled with experimental validation has provided valuable structure-activity relationships for future catalyst design: DFT calculations performed over model surfaces found that larger Ag particles promote the formation of unwanted dehydration side product, and that dispersed Ag results in directing towards the favorable formation of butadiene/butenes. DFT calculations have also indicated that n-butene formation is energetically favored over butadiene in the presence of H₂. Operando NMR was performed to clarify the reaction mechanism during n-butene-rich olefins production. Operando XPS measurements suggest the composition of product depends of the oxidation state of Ag. Catalyst lifetime studies have also indicated a major effect of the reaction environment (N₂ vs. H₂) on catalyst stability. Under N₂, the catalyst deactivates due to coking and the conversion decreases from ~92% after 6 h on stream to ~46% after 98 h on stream. However, after oxidative treatment the activity is completely recovered. Under a reducing environment the conversion is stable at ~80% for over 80 h. Overall, the Ag/ZrO₂/SiO₂ catalyst shows promise to be part of a marketable process for both butadiene and butenes-rich olefin production due to high selectivity to desired products, high stability under a reducing environment, relatively low deactivation under an inert atmosphere compared to the state-of-the-art, and catalyst regenerability.

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Deconvolution of the CO₂ Electrolysis Mechanism in Solid Oxide Electrolysis Cells with Linear and Non-linear EIS

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Carbon dioxide electrolysis will be crucial to developing an energy infrastructure with synthetic fuels produced with excess renewable energy electricity for seasonal storage or transportation.¹ Mixed ionic electronic conductors (MIEC) are a promising alternative to Ni based cathodes in solid oxide electrolysis cells because of their resistance to coking and freedom from the limitations of the triple phase boundary. Gadolinium doped ceria (GDC) been particularly well characterized as an electrolyte; however under reducing conditions GDC is an MIEC and thus a potential cathode for CO₂ electrolysis.² Traditional electrochemical techniques have offered insight into the mechanism of CO₂ electrolysis, yet there is no clear consensus on the various factors that affect the reaction.³ More can be learned by using linear electrochemical impedance spectroscopy (EIS) and the untraditional non-linear EIS (NLEIS)⁴ to probe the dependence of higher order harmonics on various factors thought to affect electrolysis. We have performed NLEIS and EIS measurements on CO₂ electrolysis under various temperatures and gas compositions. The experimental higher order harmonic impedance spectra are compared to models developed based on the two different possible rate determining steps proposed by Feng and co-workers³. The rate determining steps compared are CO₂ reduction to a carbonate and carbonate reduction to CO.

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Thermodynamics of Catalytic Materials

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High efficiency catalytic conversion of carbon-containing molecules with minimized negative environmental impacts is critical toward sustainable application of fossil energy and biofuel. Newly developed catalysts with exciting catalytic mechanisms and kinetic pathways must be stable and thoroughly understood before their qualification for industrial applications. In this regard, experimental thermodynamics studies on catalytic materials using calorimetric methodologies can provide critical information aiding the assessment of catalyst stability and surface site. Here, I present our recent calorimetric studies on several groups of catalytic materials, including transition metal ion-exchanged zeolites, noble metal-doped carbon, sulfated and metal-doped zirconia, ion-exchanged chalcogenide UCR-20, and MgO–Al₂O₃–SiO₂ ternary oxides, to elucidate the thermodynamics stability of catalyst (formation enthalpy), energetics of surface site distribution (adsorption or confinement energetics) and thermodynamics structure/composition–performance relationships. The calorimetric results obtained in these studies provide crucial energetic insights into catalyst stability and surface site distribution, and enable quantitative assessment for catalytic materials as their composition, structure, surface species evolve systematically, which will help to select catalyst candidates with potential to be applied in our energy and chemical industries.

Surface-supported cluster catalysis: Breaking the rules of conventional models in catalysis

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The population of the world is approximately 7.7 billion at present and is expected to reach 8 billion people in 2023 according to the United Nations.¹ On the other hand, CO₂ emission and population seem to move in lockstep because current energy consumption heavily relies on fossil fuels, and as a result, the global climate change threatens humankind's sustainable development.

Bioenergy with carbon capture storage (BECCS) is a rising “carbon-neutral” emission technology to address this problem which involves remediating CO₂ emissions. Among all existing reaction routes, over the past 40 years, developing heterogeneous catalysts for the efficient conversion of CO₂ to CH₃OH is still challenging due to elevated temperatures, reactivity and selectivity of such heterogeneous catalysts.² Thus new methanol production approaches or reaction systems that match the industrial CO₂ capture should be developed to address the bottleneck of the present technologies.

We designed an integrated tandem process to hydrogenate amine captured CO₂ in bioethanol solvent to methanol using the heterogeneous catalyst, a combination of Pd/C and K₃PO₄, and thus achieve negative carbon emissions. The catalytic reaction was conducted at 150 °C and 70 bar of H₂. Subsequently, about 25 % of the captured CO₂ can be hydrogenated to formate, methanol, and methane.

The integrated tandem process can convert the captured CO₂ into methanol cost-effectively in ethanol via multi-step reactions consisted of three steps: the reduction of CO₂ to formic acid, the dehydration between formic acid and ethanol to form ethyl formate, and the hydrogenolysis of ethyl formate to methanol and ethanol.

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Surface-supported cluster catalysis: Breaking the rules of conventional models in catalysis

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It has recently been shown that surface-supported nanocluster catalysts in realistic reaction conditions do not follow the conventional models used in catalysis thanks to their dynamic nature.[1–2] This opens new doors in catalysis by giving more leverage in catalyst design, but also requires a major revision of the understanding of how dynamic heterogeneous catalytic interfaces operate. We will use example of Pt supported on alumina catalyzing the reaction of dehydrogenation, characterized jointly by theory and experiment. We will demonstrate that the statistical ensemble of many (ca. 30) thermally-accessible cluster geometries in reaction conditions rather than the single global minimum structure gives a more accurate and comprehensive picture of the catalytic system. Once the description is expanded toward the ensemble, size-dependent catalytic activity is easily explained.[3] Clusters easily isomerize with low barriers in temperatures of reaction.[4] We then proposed and confirmed several doping strategies to control the selectivity of dehydrogenation,[5–6] but again, the agreement with experiment was only possible when multiple catalyst states were included in the description. The catalytic activity and selectivity of such dynamic catalysts are driven by rare and metastable catalyst states, and thus, reaction thermodynamics and kinetics are controlled by different states of the catalyst. Broken scaling relationships follow out of these specifics, as will be demonstrated on the example of graphene-deposited Pt clusters in oxygen reduction reaction (ORR).[7] Therefore, the catalyst state(s) that might not be present in the as-prepared catalyst, and rather would develop in the reaction conditions and would have the desired activity should be considered in the calculations. For instance, while Pt₇ and Pt₈ on alumina have very similar prismatic global minimum geometries, Pt₇ at higher temperatures also has access to more active single-layer isomers, which makes Pt₇ much more active than Pt₈ toward ethylene dehydrogenation reaction. This highly fluxional behavior, ensemble nature, and rule-breaking is commonplace for clusters and contrasts them to extended surfaces.

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The mechanism of intermediate of CO₂ hydrogenation to methanol

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Studies show that fossil fuels still the main source of energy result in more than 4 Gton of carbon per year had been let out to the atmosphere.[1] CO₂ hydrogenation to methanol has relatively matured in gas phase reaction with Cu loaded catalysts whether in technology nor mechanism.[2], [3] Nevertheless, it still needs cruel reaction conditions but it is unfavorable for methanol forming.[1]–[4] Right now, the homogenous catalysts for CO₂ hydrogenation involve in liquid or condensed phase convert CO₂ at a low temperature has performed an excellent activity.[5] However, the separation process is a tremendous challenge after the reaction. Comparing to the homogenous catalysts, heterogenous catalysts could solve this problem perfectly and achieve the hydrogenation process under many mild conditions than gas phase reaction.[1] Conversion of CO₂ to methanol suffer from low yield in liquid phase. Herein as the intermediate of this process, ethyl formate can be used to studied as model reaction. This paper reports that ethyl formate can be converted to methanol over a Cu based catalyst. The effects of reaction conditions, including temperature, hydrogen pressure, copper loading and different supports. On the conversion of ethyl formate and the corresponding yields of methanol have been investigated. Molar yields of methanol and methane are up to 52.88% and 6.65% respectively, under the investigated reaction conditions and with the Cu/ZrO₂ catalyst.

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Electrochemical CO₂ reduction to C₂ hydrocarbons by Cu nanofoams

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Converting CO₂ to active carbon compounds, such as CO, formic acid, methanol and other hydrocarbons is considered an essential approach to sustainable development of fuels and chemicals. Recent studies have centered on CO₂ capture, secure storage, and chemical conversions. Among various chemical reactions studied, electrochemical reduction is considered a potentially efficient way to convert CO₂ selectively into CO or other hydrocarbon fuels over metal electrodes. Among all the metals tested for the electrochemical reduction of CO₂, copper is the most attractive for its catalytic reduction of CO₂ to various hydrocarbons. Herein, we present the electrochemical reduction of CO₂ to formate and ethanol by Cu nanofoams. The reduction reaction was tested in aqueous solution of potassium bicarbonate. The working electrode was prepared by the deposition of Cu nanofoams over carbon paper via spray method. The electrocatalysis was performed at various potentials (-1.1 V to -1.7 V vs. RHE) and the reduction was found to be potential dependent. Cu nanofoam can reduce CO₂ to between at -1.1V to -1.5V. At higher voltage, ethanol production can be observed. Our studies show that Cu nanofoams when properly synthesized and activated are selective for electrochemical reduction of CO₂ to formate and ethanol.

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