

# **Invited: Predicting Catalytic Properties of Transition Metal Nano Particles – Effects of Local Morphology and Atomic Composition**

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Metallic nanoparticles are widely used in catalytic and energy applications because they present a tunable space of configurations, which together with synergistic effects between component metals can influence the overall energetics of chemical reactions. A subset of these energies function as thermochemical reactivity descriptors in derived screening models and such models have successfully helped in the design of composite metallic catalysts for numerous catalytic applications <sup>[1-5]</sup>. In this approach surface adsorption energies are used to describe reactivity in a forward design scheme with an evident lack in site-by-site resolution, thus rendering it incapable of predicting active site architectures with atomic level precision. Incorporating such specificity enhances flexibility in materials space through targeted engineering of sites possessing optimal energetics, while simultaneously explicitly accounting for stability phenomena such as surface segregation, sintering and support effects for mono- as well as multi-metallic catalysts.<sup>[6,7]</sup> In this presentation I will introduce a framework built on relations between metal atoms and metal-adsorbate complexes that directly estimates molecular adsorption energies, while systematically quantifying the effects of modifications in morphology and chemical ordering. I will discuss potential applications of this approach in nano-engineering active sites with atomic resolution, to discover the next generation of metallic catalysts.

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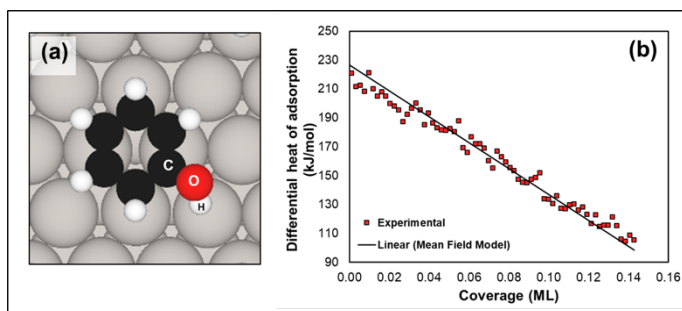
# Elucidating the Effect of the Lateral Interactions on the Adsorption of Bio-Oil Model Compounds on Pt (111)

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Biofuels have gained attention as a long-term, environmentally friendly alternative energy source that has the potential to meet the increasing energy demands from a growing world population. However, bio-oil produced from lignocellulosic biomass are of lower quality and need to be upgraded to liquid fuels through the catalytic hydro-deoxygenation (HDO) process [1]. Currently, the HDO mechanism is usually studied at low to medium coverages, for which there are no adsorbate-adsorbate interactions. However, such interactions can affect the chemical kinetics to a great extent.[2, 3] Therefore, it is important to understand not only the effect of the substrate on key HDO ad-species, but also the lateral interaction between ad-species in order to get a clear picture of the surface under realistic reaction conditions.

In this work, we use density functional theory (DFT) to model the coverage dependent adsorption energetics of phenol on Pt (111). Several adsorption sites were tested that varied both the ring position and the functional group position over the surface. Our results show that the phenol adsorption energy varies fairly linearly with the coverage for all the adsorption configurations however, near saturation the adsorption of phenol slightly deviates from its linear behavior. This could be the result of stronger through-space phenol-phenol repulsions at higher coverages as compared to low coverages where such interactions are almost negligible due to the high separation between the ad-species. These through-space repulsions are manifested through a decrease in the dihedral CO bond angle, which decreases from  $111^\circ$  to  $107^\circ$  as the nearest distance between the adsorbates decreases from  $8.8 \text{ \AA}$  to  $1.9 \text{ \AA}$ . From these adsorption energies, we then compute the average differential heat of adsorption, which agrees well with the corresponding experimental data, as shown in **Figure 1**. [4] This comparison shows that we have accurately captured the coverage dependent adsorption energetics of phenol on Pt (111) within a mean-field model. Since a mean field model can also be applied for the adsorption of benzene on Pt(111),[5] this also indicates that such a mean field model can be extended to other aromatic molecules of interest. As such, it provides a simple method for including coverage effects into micro-kinetic models, thereby making such models significantly more realistic. Overall, this work will have a large influence on the current state-of-the-art in modeling in HDO surface



reactions by allowing the use of simple models to incorporate coverage effects for large, aromatic compounds.

**Figure 1.** Adsorption of phenol on Pt (111). (a) Most favorable adsorption site. (b) Comparison between the differential heat of adsorption as obtained in a mean field model and the experimental data.

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## **Invited:** Where experiments meet computational catalysis

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Better catalysts and electro-catalysts are essential for many energy and environmental technologies of the future. Computational catalysis will surely play a huge role in guiding the search for these, but experiments will also be crucial. Recent contributions of our group to this effort will be reviewed. These include calorimetric measurements of adsorption energies of catalytic reaction intermediates on single crystal metal surfaces and of late transition metal atoms on single crystal oxide surfaces, which serve as benchmarks to guide the improvement of new DFT functionals to achieve better energy accuracy. The latter energies, when integrated over full coverage, also provide the adhesion energy ( $E_{\text{adh}}$ ) at the interface between metal nanoparticles and oxide supports, and the chemical potential of metal atoms ( $\gamma_{\text{m}}$ ) in supported nanoparticles. This chemical potential enters directly into the rate equations for catalyst deactivation by sintering, and also correlates strongly with the chemical reactivity of the surface metal atoms. Recent theoretical contributions from our group will also be described. These include a new equation describing the effect of nanoparticle size on chemical potential which replaces the Gibbs-Thomson relation (for un-supported particles) with a new term involving the strength of metal/support attractions ( $E_{\text{adh}}$ ). We also describe the use of the Degree of Rate Control in evaluating kinetic isotope effects and in designing better catalysts.

Work supported by NSF and DOE-OBES Chemical Sciences Division.

# Effects of Morphology and Dopants on the CO<sub>2</sub> Capacity of Nanofibrous Calcium-Oxide Based Materials for Sorption-Enhanced Steam Methane Reforming

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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. The primary drawbacks of SE-SMR materials are incomplete carbonation, slow carbonation kinetics, loss in activity upon cycling, and high regeneration temperature.

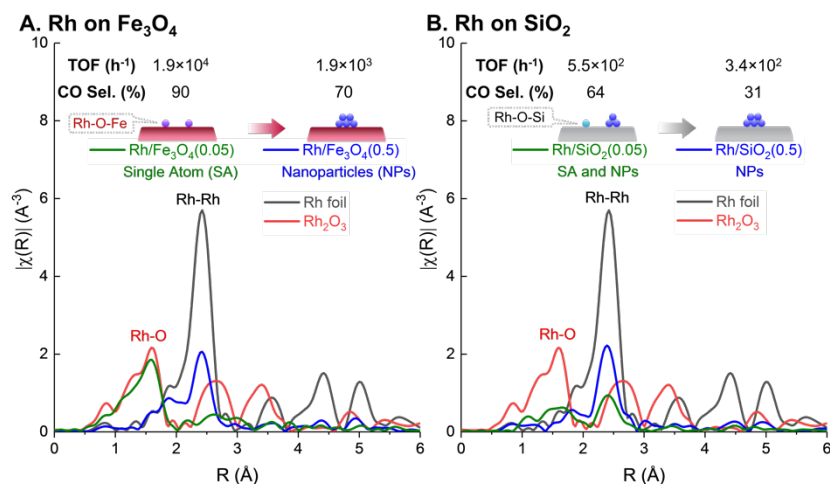
Nanofibrous calcium oxide, synthesized via electrospinning, was compared against calcium oxide synthesized via calcium acetate decomposition, hydrothermal synthesis with the aid of a surfactant, and natural sources. A thermogravimetric analyzer found that the sorption capacity of calcium oxide from nanofibers, from acetate, via hydrothermal, and from natural sources are 0.79, 0.70, 0.57, and 0.14g CO<sub>2</sub>/g sorbant after 1 hour at 600°C, 1 atm, and 100% CO<sub>2</sub>. 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. Despite that, in the SE-SMR process, the enhanced activity of calcium oxide nanofibers resulted in a breakthrough time, which was twice that of calcium oxide from natural sources. SEM, TEM, XRD, and BET were used to characterize the sorbents to identify the properties that directly influence the sorption properties such as overall capacity, kinetics, and stability.

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. After reacting these doped-sorbents at 600°C and 1 atm with 100% CO<sub>2</sub>, the added metals were shown to have various effects on capacity, kinetics, and stability. XRD was used to identify how the dopants affect the crystal structure of calcium oxide, the dopant either forms a pure oxide crystal structure or it forms a mixed metal oxide. SEM was also used to identify morphological changes in the nanofibrous structures. The results demonstrate a promising opportunity for the application of doped electrospun materials in SE-SMR.

# From Single Atoms to Clusters, Manipulating CO<sub>2</sub> Reduction Pathways on Rh catalysts

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Single metal atoms, stabilized by oxides, are attracting growing interests because of their intrinsic high metal utilization and unique catalytic behaviors.

Understanding better the hydrogenation functionality of such kind of catalysts will provide a valuable tool for engineering active catalytic sites. Herein, using CO<sub>2</sub> hydrogenation as research theme, we hypothesized that

controlling the environment and nuclearity of Rh would allow to control catalytic pathways through manipulating C-O cleavage and hydrogenation rates. Thus, a series of Rh catalysts with varying loadings were prepared on Fe<sub>3</sub>O<sub>4</sub> and SiO<sub>2</sub> following strategies based on electrostatic interactions and on cationic replacement driven by reduction potentials. According to EXAFS and HAAD-STEM, single Rh atoms are stabilized on Fe<sub>3</sub>O<sub>4</sub> in an Rh-O-Fe environment at low Rh loadings, whereas Rh clusters form at high loadings (in the 0.05-0.5 wt. % Rh range). Particle size and morphology vary with the synthesis method and support.

Single Rh atoms on Fe<sub>3</sub>O<sub>4</sub> have an intrinsic activity one- to two-orders of magnitude higher than Rh particles/clusters on Fe<sub>3</sub>O<sub>4</sub> and SiO<sub>2</sub> for CO<sub>2</sub> hydrogenation. The presence of Rh-O-Fe bonds seems mandatory to achieve such extraordinary increase in rates. Kinetic experiments performed at atmospheric pressure show that the product distribution shifts from CO/CH<sub>4</sub> mixtures to CO with nuclearity decreasing from particles to single atoms. Pressures higher than 5 atm favor C-C coupling.

Thus, the ability of Rh to hydrogenate adsorbed CO<sub>2</sub> or CO (hypothesized as the key intermediate) decreases when decreasing its metal character. However, the ionic environment of the Rh-O-Fe sites gives them a strong affinity with CO<sub>2</sub>, which enhances the reduction rates. Quantification of this fundamental understanding will enable precise predictions of catalytic performance in function of rational design.

**Invited:** Mapping the water-gas shift reaction network over an oxide-supported transition metal catalyst using operando infrared spectroscopy

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Embroiled in controversy for decades, definitive mechanistic proof for the catalytic pathway during low-temperature water-gas shift remains elusive. Our limited understanding inhibits the development of catalysts with high operational output, ultimately delaying our progress toward a more sustainable future. I will discuss recent mechanistic findings for this technologically important reaction through our studies of the reverse water-gas shift (rWGS) over Pd/Al<sub>2</sub>O<sub>3</sub> using operando infrared spectroscopy. Our results provide a holistic clarification for the intermediates commonly observed and not observed during shift catalysis, which have been the primary cause for the decades-long mechanistic controversy. Moreover, we provide definitive experimental evidence for a rate-determining step previously unidentified both experimentally and computationally. The generality of this rate-determining step suggests it is mechanistically relevant to other high-temperature hydrogenation reactions, especially those that involve oxygenates. Finally, we were able to delineate a site-selectivity relationship for regioselective and chemoselective H-addition to CO<sub>2</sub> that yields the active intermediate. The new mechanistic insight provides a unified explanation to disparate literature results still permeating the field and offers a detailed roadmap for the rational design of catalysts showing high shift activity.

**Acknowledgement:** This research was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences.

# Kinetic and Mechanism Studies for Alcohol Dehydration over Zeolites in Apolar Solvent

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Alkenes play crucial roles in organic synthesis to produce valuable chemicals including polymers, drug molecules and valuable building blocks. Although many methods have been developed to synthesize alkenes, direct acid catalyzed dehydration of alcohols to form C=C bonds are efficient and environment friendly with water as sole by-product. When this reaction proceeds within the pores of microporous materials, confinement effects greatly influence the intrinsic activity of the hydronium ion and reaction mechanisms.<sup>[1-2]</sup> The detailed understanding of its mechanism in liquid-solid phase is still urgent and key for catalysts design and innovation in biomass conversions. We performed the dehydration of cyclohexanol over zeolites with varying pore diameters (0.55 to 0.74 nm). The free-energy barriers for dehydration could be reduced by employing apolar solvents like decalin instead of aqueous phase. Kinetic results disclose that activities of monomeric cyclohexanol dehydration over three zeolites far exceed those of dimer intermediate. The mechanism studies including <sup>2</sup>H NMR and kinetic isotope effect (KIE) experiments reveal that the C-O bond cleavage is the rate determining step for cyclohexanol dehydration over zeolites through E1 elimination.

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## **Invited:** Ultra-Deep Diesel Hydrodesulfurization Catalysis and Process: A Tale of Two Sites

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Hydrodesulfurization catalysts have two types of active sites for hydrogenation and hydrogenolysis reactions. While hydrogenation sites are more active for desulfurizing refractory sulfur species, they are more vulnerable to organonitrogen inhibition than hydrogenolysis sites. In contrast, hydrogenolysis sites are less active for desulfurizing refractory sulfur species but are more resistant to organonitrogen inhibition. This dichotomy is exploited to develop an ultra-deep hydrodesulfurization stacked-bed reactor comprising two catalysts of different characteristics. The performance of this catalyst system can be superior or inferior to that of either catalyst alone. A theory is developed to predict the optimum stacking configuration for maximum synergies between the two catalysts. The best configuration provides the precise environment for the catalysts to reach their full potentials, resulting in the smallest reactor volume and maximum energy saving. Model predictions are consistent with experimental results. A selectivity-activity diagram is developed for guiding the development of stacked-bed catalyst systems.

# Catalysis in Biomass Upgrading: Fundamental and Applied Insights into the Production of Diesel Fuel Replacements

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The successful implementation of the biorefinery concept requires the development of pathways to produce a broad range of fuels and chemicals from biomass. In this talk, a novel method to produce diesel fuel from non-food biomass sources will be presented. In this, fermentation-derived mixtures of ethanol, butanol and acetone (ABE) are upgraded to diesel fuel precursor ketones via a tandem catalytic dehydrogenation and aldol condensation sequence over bifunctional metal and basic catalysts.

In this process, the key to achieving high selectivity is the prevention of decarbonylation reactions of the reactive aldehyde intermediates, a reaction that takes place over group VIII B metals, such as Ni, Pd and Pt. To solve this challenge, alloys of Pd and Cu are used as catalysts. Kinetic experiments show the prevention of decarbonylation by the alloying, while X-ray absorption spectroscopy data indicate that Cu overlayers are formed on top of Pd nanoparticles. Density functional theory calculations indicate these overlayers prevent the binding of alkyl and carbonyl species onto the surface, thereby preventing decarbonylation. Combining the insights of spectroscopic, kinetic and theoretical investigations, a selective catalyst for the ABE upgrade process is developed. Further experimental and theoretical investigations of the intrinsic kinetics of the decarbonylation and (de)hydrogenation reactions reveal that CO coverage of the surface enhances the (de)hydrogenation selectivity. Furthermore, we find that the decarbonylation of butyraldehyde proceeds on Pd-Pd ensembles while hydrogenation and dehydrogenation reactions take place over Pd-Cu ensembles. Last but not least, the investigation of particle size effects afford a unified picture of hydrogenation and decarbonylation reactions for Pd and PdCu catalysts: stronger binding of alkyl and carbonyl fragments results in enhanced decarbonylation reactivity at the expense of (de)hydrogenation.

# Bimolecular Condensation of Alcohols over Hydroxyapatite: Mechanisms and Site Requirements of C-C and C-N Bond Forming Reactions

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Light oxygenates derived from petrochemical processes or renewable sources can be used as synthons to make high-value products. Currently, there is a need to develop more active and selective catalysts for these reactions. Our research focuses on understanding the mechanisms and site requirements of C-C and C-N coupling of light oxygenates.

The bimolecular condensation of ethanol to n-butanol was investigated over hydroxyapatite (HAP), which demonstrates an unusually high activity and selectivity (>80%) to butanol. Steady-state, gas-phase kinetic studies over HAP reveal that the mechanism proceeds through a Guerbet pathway, in which ethanol dehydrogenates to form acetaldehyde, acetaldehyde undergoes aldol condensation to form crotonaldehyde, and crotonaldehyde is hydrogenated to form butanol. The reaction is autocatalytic with respect to acetaldehyde, which can be explained by the rapid hydrogen transfer reaction that occurs between crotonaldehyde and ethanol to form butanol and acetaldehyde. A combination of spectroscopic studies and in-situ titration experiments suggest that ethanol dehydrogenation is catalyzed over Ca-O sites on HAP while aldol condensation requires CaO/PO<sub>4</sub><sup>3-</sup> pairs.

The dehydroamination of alcohols to amines was also investigated. The dehydroamination pathway is very similar to the Guerbet pathway, suggesting that the insights gained from the previous study can be applied here to design an active amination catalyst. The initial dehydrogenation step was found to be rate-limiting over HAP. The energy barrier can be lowered by adding a transition metal, which increases reaction rates by an order of magnitude. Ni/HAP was found to be more active and selective towards the primary amine compared to Ni/SiO<sub>2</sub>, highlighting the importance of the acid/base properties of the support. Turnover frequencies are invariant with Ni particle size when normalized by the number of perimeter Ni atoms, showing that the active sites for dehydrogenation are located at the interface of metal and support.

**Invited:** Changing Paradigms in the Fischer Tropsch Reaction Mechanism of long-chain Hydrocarbon Production from Carbon Monoxide and Hydrogen

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Despite extensive studies of the catalytic CO hydrogenation according to Fischer Tropsch (FT), a detailed understanding of the reaction mechanism leading to long-chain hydrocarbons is still missing. C-C coupling and CO-insertion remain the two main mechanisms considered for the reaction. The present contribution aims to scrutinize which mechanism would be compatible with more recent experimental results obtained by using operando-type Chemical Transient Kinetics (CTK).

Chemical transients provide relaxation-type information on the response behavior of catalysts relative to abrupt changes of the gas phase composition. Our studies with Co/MgO and Co/MnO<sub>x</sub> allowed the atomic amounts of surface carbon, oxygen and hydrogen, while constructing the catalytically active surface (“build-up”), to be evaluated for the CO hydrogenation under atmospheric pressure conditions. This way, it was shown that the monolayer limit was largely surpassed for both types of catalysts before they reached steady state. Thus, the surfaces of these catalysts did not provide metallic sites for chain lengthening to occur. Furthermore, for the above catalyst systems, C<sub>2+</sub> hydrocarbons appeared in sequence with considerable delay times after initiating the reaction. In the case of Co/MnO<sub>x</sub> catalysts, olefins were produced with high selectivity *after* triggering alkane formation. This excludes the possibility of considering alkanes as being formed by simple hydrogenation of olefins. Generally, chain lengthening was hardly ever observed under conditions of irreversible CO chemisorption. Instead, gaseous CO was necessary for this to occur. This behavior was interpreted as being in agreement with a CO insertion mechanism. This interpretation was supported by the finding that during back-transients (removal of CO gas from the reactive CO/H<sub>2</sub> mixture), CO was seen to disappear from the reactor with the same time constant as the Ar reference gas. Last, but not least, plotting the Anderson-Schulz-Flory (ASF) chain lengthening probability for hydrocarbon formation during build-up clearly showed proportionality to the transient CO pressure. Such proportionality was not found for accumulating carbon (or CH<sub>x</sub>) as would be expected if CH<sub>x</sub> insertion or C-C coupling were occurring.

DRIFTS showed the formation of surface formate species for both types of catalyst. To clarify the question for the role of such species as intermediates of the FT reaction, we performed hydrogenation measurements using methyl formate (CH(O)OCH<sub>3</sub>) rather than CO. Interestingly, very similar CTK time patterns were found, indicating formate-type species are indeed involved in the hydrocarbon chain lengthening mechanism. Strikingly, the ASF chain lengthening probability was once again directly proportional to the CO transient pressures evolving during methyl formate decomposition on the catalyst surface.

Finally, a formate-type mechanism of the FT reaction will be presented and discussed in the light of the available experimental evidence gained through combined CTK/DRIFTS studies.

## Bipolar junction anionic thin layer water electrolyzers

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Proton exchange membrane electrolyzer exhibit high current density, differential pressure and elevated temperature operation, which is supported by the acidic electrolyte membranes, such as Nafion. However, the oxygen evolution reaction in the acidic environment requires expensive precious metal catalysts. Here, we embed the oxygen evolution reaction catalyst in a basic local environment by utilising a thin anion exchange ionomer layer while still relying on conductive and stable Nafion for the product separation and mechanical robustness. Compared to regular bipolar membranes which use thick anion exchange membranes, the thin anion exchange ionomer layer ensures improved ionic conductance and improved water supply to the water-dissociating bipolar junction. The devices using such a geometry (1-2  $\mu\text{m}$  FAA-3|50  $\mu\text{m}$  Nafion) support initially an electrolysis current density of 200  $\text{mA cm}^{-2}$  at an applied voltage of  $\sim 2$  V, while maintaining the catalyst material in an alkaline environment. After the initial polarization curves, we observe a substantial improvement; current densities of 200  $\text{mA cm}^{-2}$  at  $\sim 1.7$  V are obtained. We propose possible mechanisms leading to the pronounced change over time. Bipolar junction anionic thin layer geometries are a promising route to integrate local alkaline catalyst environments into compact electrolyzer architectures, without sacrificing efficient ionic conductance and water transport.

**Invited: TDB**

Thomas Bligaard  
SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory,  
Stanford University

## Posters:

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### A Dft Study Of Hydrodeoxygenation Reaction Mechanism

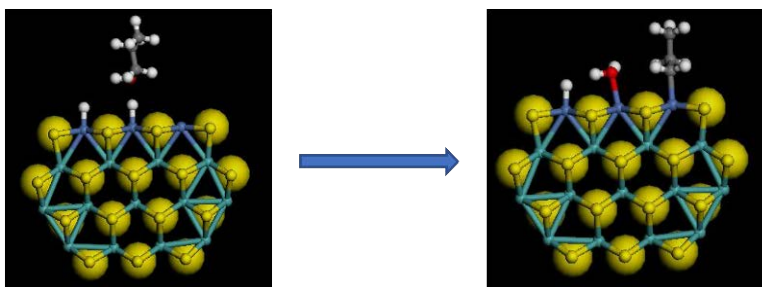
Dan Huang<sup>1</sup>, Matthew Coblyn<sup>1</sup>, Bavornpon Jansang<sup>2</sup>, Nichaporn Sirimungkalakul<sup>2</sup>, Thana Sornchamni<sup>2</sup> and Goran Jovanovic<sup>1</sup>

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Energy consumption increases each year and consumption of distillate fuel oil, an important energy source, increased 93% from 1986 to 2012.<sup>1</sup> Additionally, worldwide carbon dioxide emissions increase yearly, contributing to the greenhouse effect. Alternative and renewable diesel, derived from vegetable oils such as rapeseed, soybean oil, sunflower oil, palm oil and waste cooking, have been proposed to meet the increasing diesel fuel demand while reducing associated carbon dioxide emissions.<sup>2,3</sup> Bio-hydrogenated diesel is generated via hydrogenation of triglycerides and the main product components are alkanes which is the same as normal fossil diesel. One of the primary reaction mechanisms is hydrodeoxygenation (HDO). Many researchers have been trying to elucidate the HDO reaction mechanism via experimental measurement. However, detection limitations and short lifespans of intermediates make it difficult to determine the true reaction mechanism.

In this work, DFT was used to investigate the HDO reaction mechanism, with a focus on the reaction of propanal to propane. Propanal was chosen as the molecule to study since it is a key intermediate for two main competing reaction mechanisms (HDO and HDC) in renewable diesel production. Additionally, given the high activity of aldehyde, it is hard to detect it in experiments.<sup>4</sup> Therefore, DFT studies are critical to understanding its precise role during the hydrodeoxygenation reaction. The results indicate that the kinetically favored route includes 1) hydrogenation of propanal into propanol, 2) C-O bond cleavage of propanol and 3) propane formation. The critical elementary step is hydrogen assisted C-O bond cleavage (scheme below).



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# Surface Chemistry of 2-Propanol on SnO<sub>2</sub>(110) Studied with Ambient-Pressure X-ray Photoelectron Spectroscopy

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Tin dioxide (SnO<sub>2</sub>) has a wide range of applications, including gas sensors, transparent conductors, and oxidation catalysts.<sup>1</sup> The surface chemistries for each of these applications can be strongly influenced by the surface chemistry and cation oxidation states. The oxidation of volatile organic compounds (VOC) has recently been demonstrated using SnO<sub>2</sub>, where 2-propanol was used as the probe molecule.<sup>2</sup> Recently, carbon monoxide oxidation has been studied, where the Sn<sup>2+</sup>/Sn<sup>4+</sup> ratio strongly influenced the activity of the catalyst.<sup>3</sup> In this study we have used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to characterize the surface chemistry of 2-propanol on well-defined SnO<sub>2</sub>(110) surfaces. We have prepared stoichiometric and reduced surfaces which were characterized with AP-XPS and low energy electron diffraction. AP-XPS was performed on both surfaces for 2-propanol pressures up to 1 mbar. These measurements allowed us to determine the chemical states of 2-propanol on the SnO<sub>2</sub>(110) surface. The effect of sample temperature during exposure was also evaluated. We have found that both the Sn<sup>2+</sup>/Sn<sup>4+</sup> ratio and sample temperature strongly influence the surface chemistry. Additionally, we have developed a mechanism that describes the oxidation of 2-propanol on SnO<sub>2</sub>(110) surfaces.

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# Mechanistic Study of Oxygen-Reduction activity on Fe substitution LaCoO<sub>3</sub> Electrocatalysts

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Recent decades, the scarcity of fossil fuels and global warming drive the development in green and renewable energy resources. Some new technologies such as metal-air batteries, water electrolysis and fuel cells that are based on the electrochemical oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are promising devices for the sustainable development using clean energies. However, the low efficiencies of ORR and OER prevent the commercialization of such device and the search for platinum group free metal oxides such as LaCoO<sub>3</sub> are needed. Our study focuses on a series of Fe substituted LaCoO<sub>3</sub> as electrocatalysts for both OER and ORR. A combination of hard as well as soft X-ray characterizations and electrochemical performance demonstrated the importance of Co 3d electronic structure and Co (3d)-O (2p) hybridization in OER and ORR. We thus proposed a reaction mechanism related to our catalysts, which can potentially expand to other oxide-based bi-catalysts for electrolyzers and fuel cells.

## Process intensification efforts for efficient, modular production of low carbon intensity liquid fuels

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Intermittent solar availability limits the applicability and economic appeal of solar energy. Thus, a clean energy future for humanity will depend on sophisticated approaches to storing solar energy. Solar thermochemical energy storage is one such approach that shows promise of generating practical liquid fuels. Concentrated solar irradiance provides high temperatures that can drive highly endothermic reactions, storing solar energy in the form of chemical bonds. Here, the design of a microscale based, thermally coupled reactor/solar receiver is explored. It is the intention of this device to reform methane in the presence of flue gas and to subsequently process syngas directly into liquid fuels. A recuperative, counter flow design is employed to increase thermal and exergetic efficiencies, and it is hypothesized that thermally coupling an endothermic and exothermic reaction in series by judicious orientation of catalyst in the reactor will further increase thermal efficiency.

# Modeling the Reaction Mechanism of Carbon Monoxide Oxidation on a Clean and an Oxidized Cu(110) Surface: A Density Functional Theory Study

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Carbon monoxide (CO) oxidation is a very important reaction used in automobile emissions control due to the need to convert incompletely combusted CO into a less directly toxic product, CO<sub>2</sub>. It also plays a role in other chemical processes such as the water gas shift reaction, which produces hydrogen gas, an important component of fuel cells [1]. By theoretically modeling a catalytic surface for this reaction, we can work to fundamentally develop a catalyst that lowers the reaction temperature necessary for carbon monoxide oxidation. This can potentially address challenges faced by low-temperature combustion engines. It is known experimentally that the oxidation of carbon monoxide takes place on a clean Cu(110) surface, though there has not been any theoretical study of the mechanistic path [2]. Using density functional theory implemented in the Vienna *ab initio* Simulation Package (VASP), we can map out the reaction pathway for oxidation over this relatively simple surface. Once well-defined, we can begin to characterize the reaction over isolated metal dopants incorporated into the Cu(110) surface as well as over an oxidized Cu(110) surface. As both types of systems have recently shown great potential in reactivity compared to traditional catalysts [3, 4], this work will provide needed insights toward the design of new “single-site” catalysts that can be utilized in the chemical and automobile industries.

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# Effects of step edges on Cl interactions with $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> surface: A Density function theory study

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A protective oxide film (passive film) is formed on the surface of iron in highly alkaline environment, such as inside reinforced concrete. Experiments have shown that Cl can induce breakdown (depassivation) of the passive film under the same condition. Several hypotheses have been proposed to explain chloride induced depassivation such as ion exchange model and point defect model, but the atomistic mechanism of depassivation is still not fully understood. Here we use density functional theory to investigate the role of chloride in the depassivation process.

The dominant oxides in the outer layer of the iron passive film are Fe (III) rich oxides, which is represented here using hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). The energetics of two different depassivation models, ion exchange and point defect models are compared. The ion exchange model assumes a diffusion of Cl into the bulk but no exothermic insertion of Cl into the bulk was identified on the flat surface. The point defect model, on the other hand, assumes depassivation driven by vacancies diffusion and Cl can assist with the surface Fe vacancy formation. We have previously shown Cl enhanced Fe vacancy formation mechanism as well as thermodynamic favorable diffusion of both O and Fe vacancies on the flat surfaces and here we extend our study to step edges and defect sites. The study showed that the adsorption of Cl is strongly affected by the step sites but the effect mostly dies out beyond two Fe atoms from the step edge. The insertion of Cl into the stepped surface was found to be unfavorable same as the flat surfaces, making the mechanism explained by the ion exchange model an unlikely even on steps and defects sites. The effects of step edges on the Fe vacancy formation will be discussed.

Work supported by NSF CMMI.

# Density Functional Theory and Ambient Pressure XPS Study of Solvent Effects in the Decomposition of Acetic Acid

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Heterogeneous catalytic reactions play an important role in the production of fuels, chemical synthesis, exhaust clean up, and pharmaceuticals. Many of these reactions occur in ambient conditions, high pressures, or in the presence of a liquid solvent. Most of our atomistic understanding of these catalytic reactions comes from surface science studies in ultrahigh vacuum. In this work we start bridging the gap between ultrahigh vacuum and industrial conditions by combining near ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) and density functional theory (DFT). NAP-XPS is used to confirm theoretical results through the analysis of chemical shifts of the carbon 1s binding state and quantification of elemental composition at a range of pressures from ultra-high vacuum to approximately 25 mbar. DFT is used to calculate binding energies, reaction energies, and transition states, both in vacuum conditions and in the presence of solvents. The solvent effect calculations are performed through a combination of implicit solvent methods (VASPsol) and addition of individual water molecules to each elementary step in the reaction pathway. Combining explicit and implicit methods can reduce the computational time required to model a reaction pathway without sacrificing accuracy if hydrogen bonding is modeled correctly. Final and initial state calculations of acetic acid interacting with a single water molecule have been performed to determine the most favorable configurations with different solvent models. Including implicit solvent reduces the binding energies of the acetic acid and acetate but also changes the lowest energy configuration of acetic acid. This leads to an increase in the predicted reaction energy, which is almost neutral in implicit solvent. Including explicit water molecules adds both water-surface interactions as well as hydrogen bonding between the explicit water and the adsorbate so the overall binding energies of the co-adsorbates increase. The acetate is slightly more stabilized by these interactions leading to more exothermic reaction energy. A combination of explicit and implicit solvation results in reduced binding energies and a less exothermic reaction energy compared to the vacuum system. Calculations on how solvent effects activation energies are under way. The effect of different approaches, explicit, implicit, and a combination of explicit and implicit solvation is addressed through comparison of these systems with vacuum calculations.

Work supported by NSF Chemical Catalysis.

# First-principles study of the decarboxylation and decarbonylation of acetic acid over Pd (111)

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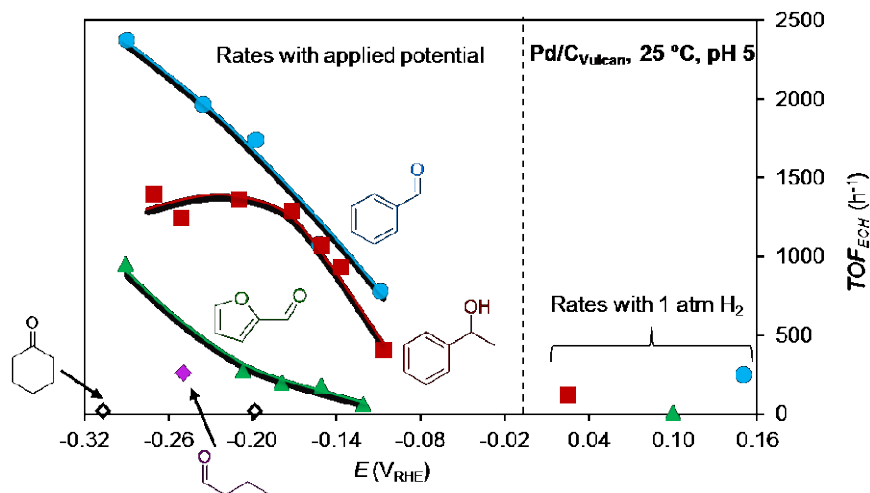
The decomposition of acetic acid on the Pd (111) surface is of both fundamental and applied interest. The interaction of acetic acid with Pd (111) is key to the production of vinyl acetate (a precursor to the important industrial polymer, polyvinyl acetate), biomass conversion to biofuels and other industrially relevant reactions. Understanding the reaction mechanism of acetic acid decomposition, at an atomic scale, can also help us design more effective catalyst and catalyst system. Here we present Density Functional Theory calculations of reaction mechanism of acetic acid decomposition on Pd (111). We investigated the elementary steps involved in for both decarboxylation(DCX) and decarbonylation(DCN) of acetic acid and identified two major pathways for DCX and DCN. Both the DCX and DCN can proceed through dehydrogenation of acetic acid( $\text{CH}_3\text{COOH}$ ) to acetate( $\text{CH}_3\text{COO}$ ) or through  $\alpha$ -carbon dehydrogenation of  $\text{CH}_3\text{COOH}$  to Methylidene-1-ol-1-olate( $\text{CH}_2\text{COOH}$ ). From the acetate, the competition between DCN and DCX pathway depends on two endothermic routes, the deoxygenation of  $\text{CH}_2\text{COO}$  to ketene ( $\text{CH}_2\text{CO}$ ) ( $E_a=0.98\text{eV}$ ) and dehydrogenation of the carboxylmethylidene ( $\text{CH}_2\text{COO}$ ) to carboxylmethylidyne ( $\text{CHCOO}$ ) ( $E_a=0.94\text{eV}$ ). Our DFT calculations suggest that  $\text{CH}_2\text{CO}$  is a stable intermediate in the decomposition of acetic acid over Pd (111). In the second major pathway through methylidene-1-ol-1-olate, the competition between DCN and DCX pathway depends on the dehydroxylation of  $\text{CCOOH}$  to  $\text{CCO}$  ( $E_a=1.42\text{eV}$ ) and dehydrogenation of  $\text{CCOOH}$  to  $\text{CCOO}$  ( $E_a=1.24\text{eV}$ ). These calculations give an insight into the complexity of decompositions of oxygenations and the interplay between the different reaction routes. Work supported by NSF Chemical Catalysis

# Reaction networks and mechanisms in electrocatalytic hydrogenation of carbonyl compounds

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Electrocatalytic hydrogenation (ECH) is a promising approach that combines the utilization of renewable electricity with the conversion of biogenic carbon sources storing energy in chemical bonds. Carbonyl groups are one of the most abundant and reactive functionalities of molecules contained in bio-oil. Hence, the stability of the treated bio-oil is improved by reducing the carbonyl content. Recent studies pertaining to ECH of benzaldehyde on different carbon supported metal catalyst demonstrated the superior activity of Pd/C compared to other catalysts (Pt/C, Rh/C, Ni/C) towards hydrogenation of carbonyl functionalities. In the present study we explore the chemistry of aqueous phase hydrogenation of different carbonyl compounds at low temperatures under the influence of electric potentials with an aim to understand the influence of molecular structure on the reaction pathways and selectivity to ECH. Series of aromatic and aliphatic carbonyl compounds have been tested on C-supported Pd. All measurements were conducted in acetate buffer (pH 5) within a cathodic potential range of -0.1 to -0.3V vs RHE. At these reaction conditions the reactivity of aromatic carbonyls is much higher than that of aliphatic ones. Aldehydes and ketones are selectively converted to alcohols, i.e. aromatic rings are unreactive. The H<sub>2</sub> evolution reaction (HER) is the only pathway competing with the hydrogenation of the organics. The ECH rates of aromatic carbonyls, as well as HER rates, increase with increasing cathodic potential and further enhancement of these rates (~ 2 fold) was noted by using acidic electrolyte (pH 2). Thermal catalytic hydrogenation (TCH) of these carbonyl compounds were also studied with 1 bar H<sub>2</sub> used as the reductant. The rates of ECH were always higher than TCH rates, which points to an electrochemical mechanism dominating the reaction. The kinetic studies as well as plausible elementary steps of carbonyl hydrogenation pathways will be discussed in detail.



## Understanding chemical interactions at solid/gas and solid/liquid interfaces

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Electrocatalysts are important constituents in numerous energy conversion and storage processes. Reactants adsorb onto the electrocatalyst surface, where the interplay of electronic states results in a lower activation barrier for the transfer of electronic and ionic species in the reaction pathway to product formation. Rational design of electrocatalysts with greater activity for higher efficiency devices requires an understanding of the material's electronic structure *in situ*, as well as the reaction intermediates involved.

We will present studies of model oxide (photo)electrodes grown by molecular beam epitaxy (MBE) on single crystal substrates that display a known crystallographic orientation, surface area, path for charge transport, and strain. Photoelectrochemical measurements on these heterostructures can establish the intrinsic activity of oxide catalysts in a way that cannot be realized with polydisperse nanoparticle systems. Insight into the band bending between the substrate and oxide overlayer, as well as at the semiconductor surface, can be obtained from X-ray photoelectron spectroscopy (XPS). Measurement of XPS at ambient pressures (AP-XPS) can further elucidate the relationship between adsorbates and surface band bending *in situ*. We will discuss the insights obtained with this technique regarding the electronic structure of perovskite oxide electrocatalysts in an oxidizing or humid environment, as well as the reaction intermediates of relevance to oxygen electrocatalysis. We will then extend the technique to probe electrocatalysts *in operando*, driving current through a thin layer of liquid electrolyte and employing a tender X-ray source. This fundamental insight will build understanding necessary for the design of active, earth-abundant photocatalysts that can be integrated into PEC devices for efficient conversion of solar energy into chemical fuels.



# Application of an improved Computational Model to the Dehydrogenation of Light Alkanes Catalyzed by Ga/H-MFI

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In this work, we use an improved computational model of Ga/H-MFI to understand both the nature of the active gallium species and the associated dehydrogenation mechanism for light alkane dehydrogenation, both of which have previously been difficult to establish using early theoretical finite cluster approximations. In order to provide a more complete picture of transition states and surface intermediates in zeolite pores than provided by such finite cluster models, both long-range interactions associated with the zeolite framework and entropic effects must be accounted for. Towards the first end, Quantum Mechanics/Molecular Mechanics (QM/MM) models, based upon additive, hybrid DFT/Force field schemes, can be used to cost-effectively capture long-range framework interactions in zeolites. In this work, we first use an improved QM/MM model which utilizes a range-corrected functional and a good representation of dispersive interactions. Furthermore, we examine the activity of Ga species in Ga/H-MFI by computation of the free energy landscapes on which all reactions occur. The rate-determining TS (RDTS) is identified by analysis of the free energy landscape for each mechanism, using the energetic span model. Our analysis reveals that, for reduced Ga/H-MFI, univalent and divalent gallium hydrides,  $[\text{GaH}_2]^+$  and  $[\text{GaH}]^{2+}$ , respectively, are more active for ethane dehydrogenation in comparison to  $\text{H}^+$  sites and  $\text{Ga}^+$  sites.  $[\text{GaH}]^{2+}$  sites consistently emerge as the most active sites for light alkane dehydrogenation, providing significant enthalpic stabilization to C–H cleavage TSs via alkyl and carbenium dehydrogenation routes. In contrast, carbenium-like C–H cleavage TSs occurring on Brønsted acid sites are enthalpically less favorable due to their limited electronic interactions with framework O atoms and  $\text{H}^+$  sites. Activation enthalpy barriers for dehydrogenation determined using the energetic span analysis are in good agreement with those measured experimentally. Accounting for entropy of activation reveals that constrained TSs become less favorable in free energy with increasing chain length. We also find that an increase in enthalpic favorability of the alkyl mechanism is observed with increasing chain length for the TS responsible for the second C–H cleavage step leading to alkene formation.

# Mechanism and Kinetics of Isobutene Production over Zinc-Zirconium Mixed Oxide

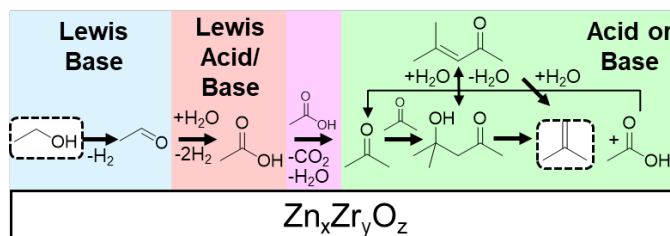
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Growing interest in producing fuels and valuable chemicals from biomass-derived feedstocks has motivated the investigation of catalytic upgrading of ethanol, acetic acid, and acetone. Recent reports in the literature have identified zinc-zirconium mixed oxides as effective and selective catalysts for the direct conversion of ethanol and acetone to isobutene, a valuable specialty chemical used in the production of polymers, fuel additives, and other high-value products. But, there are many unanswered questions pertaining to the reaction intermediates, the roles of acidic and basic sites on the surface of the catalyst, and the role of water in promoting selectivity and catalyst stability for this reaction. In this investigation, the kinetics and mechanism of the ethanol and acetone to isobutene reactions were probed in order to elucidate the reaction pathway and the active sites responsible for each step in the mechanism.

Zinc-zirconium mixed oxide catalysts with varying zinc loadings were synthesized via incipient wetness impregnation and were characterized with XRD, BET, CO<sub>2</sub>-TPD, and DRIFTS FTIR with pyridine adsorption. The zinc-zirconium mixed oxide with a Zn:Zr molar ratio of 1:10 was found to be highly selective and active for the acetone to isobutene reaction, reaching a nearly-theoretical selectivity towards isobutene of over 86% at 723 K. Kinetic studies suggested that the ethanol to isobutene reaction proceeds via dehydrogenation to acetaldehyde, followed by hydration to form acetic acid, ketonization to produce acetone, dimerization of acetone to form diacetone alcohol, reversible dehydration to form mesityl oxide, then finally either hydrolysis of mesityl oxide or cleavage of diacetone alcohol to produce isobutene and acetic acid, which undergoes further ketonization to produce acetone. Additional investigation into the roles of acidic and basic sites suggests that Lewis basic sites are required for ethanol dehydrogenation, and balanced Lewis acid/base sites are preferred for acetaldehyde hydration to acetic acid, whereas the acetone to isobutene pathway can be catalyzed by either basic or acidic sites. Understanding the reaction pathway, mechanism, and roles of the acidic and basic sites can help to define the catalyst properties required to selectively produce isobutene from a variety of sustainably-derived platform molecules.

Graphical Abstract:



# Characterizing the Binding of Phosphates on Nitrogen-Functionalized Biochars: A Combined Experimental and Theoretical Study

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The scale and intensity of human agriculture often has dire impacts on the surrounding environment, such as the eutrophication of local waters by fertilizer contamination.<sup>1</sup> Phosphate's dramatic enhancement of plant growth plays a key role in these processes, and its adsorption and sequestration are critical control measures. Biochars have been studied extensively for this role due to their easy production from agricultural byproducts and potential for re-use as soil amendments. This study aims to contribute to the field by experimentally and theoretically characterizing the adsorption of phosphate on nitrogen functionalized biochars. In order to isolate the contribution of individual components, simple cellulose chars were produced with varying combinations of nitrogen and trace metal doping. These chars were characterized using x-ray photoelectron spectroscopy and tested for adsorption capacity and kinetics. Meanwhile, corresponding density functional theory calculations were performed for phosphate species on common functional groups within the char. These simulations were used to assess the adsorption energetics, the likely mechanisms, and to support the aforementioned characterization with highly specific spectra. The result is a thoroughly vetted model of nutrient adsorption in nitrogen doped biochars developed through synergistic computational and experimental efforts.

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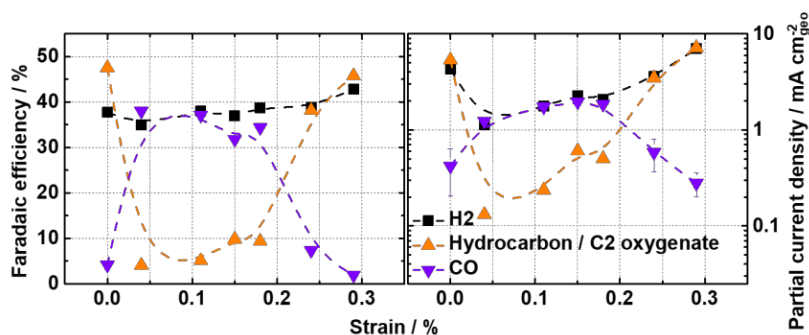
# Strain-controlled Electrochemical CO<sub>2</sub> Reduction to Hydrocarbons and Oxygenates on Planar Copper

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In this study, we introduce tensile strain on planar polycrystalline copper electrodes mechanically and observe significant changes in the selectivity of aqueous CO<sub>2</sub> reduction, indicative of changes in the binding energy of key intermediates. Copper is one of the few CO<sub>2</sub> reduction catalysts where hydrocarbons and oxygenates can be produced with reasonable activity, but poor selectivity is a significant challenge. There is considerable interest in engineering copper to tune CO<sub>2</sub> reduction selectivity by modifying surface morphology<sup>1</sup> or alloying with other metals.<sup>2,3</sup> Recent studies more broadly in electrocatalysis also demonstrate that elastic strain can influence the activity of catalytic surfaces.<sup>4–6</sup>

We observe that the magnitude of the tensile strain applied to the planar copper electrode strongly governs the CO<sub>2</sub> reduction selectivity towards hydrocarbons (methane and ethylene) and C<sub>2</sub> oxygenates (ethanol and acetate). For example, at -1.1 V vs RHE, where higher reduction products can be formed, it appears that the strongest tradeoff is the formation of CO in place of CH<sub>4</sub> in the range of strain from 0.04 to 0.18%. This tradeoff likely indicates a change in CO binding energy, one of the best descriptors of CO<sub>2</sub> reduction to hydrocarbons and oxygenates. These findings provide evidence for strain engineering as a tunable approach to modifying the surface binding energy of CO<sub>2</sub> reduction intermediates. We will describe our latest understanding of the changes in surface chemistry that strain introduces, offering the potential to tailor the design of high surface-area electrocatalysts with enhanced selectivity for CO<sub>2</sub> reduction.



**Figure.** Strain-controlled electrochemical CO<sub>2</sub> reduction at -1.1 V vs RHE in 0.1 M KHCO<sub>3</sub> and 0.6 M KCl solution. (a) Faradaic Efficiency and (b) Geometric partial current density with respect to tensile strain applied.

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# *In Situ* Studies of Electrocatalyst for Oxygen Evolution Reaction in Acidic Condition Using A Combination of X-ray Scattering and Spectroscopy

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Exploitation of fossil energy has increased the atmospheric CO<sub>2</sub> concentration, which leads to severe climatic problems. Clean fuels such hydrogen and oxygen produced from water splitting provide alternative solutions for green energy conversion and production. However, since the efficiency of the water splitting reaction is largely limited by the high overpotential required by the oxygen evolution reaction (OER) and the relatively slow kinetics of the OER, high-performance and stable electrocatalysts are required. As the electrocatalytic reactions strongly depend on the surface atomic structures of the electrocatalysts, in this work, we have combined *in situ* X-ray diffraction and X-ray absorption spectroscopy to study nanocatalysts that consist of a Pd core in a IrO<sub>2</sub> shell with two different surface morphologies, namely one with a flat surface and the other with a concave surface. We found that the concave sample undergoes atomic structural and oxidation state changes during the process while the flat one showed no change. In addition, cyclic voltammetry tests conducted on both concave and flat samples reveal that concave sample shows a relatively lower overpotential compared to the flat sample. Our *in situ* measurements can be correlated with their stability and activity and the insights learned from this study can provide ways to design and control cost-effective and efficient catalysts for OER.