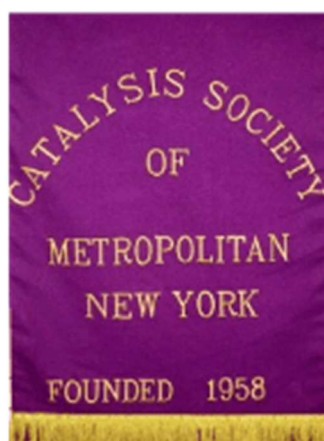


The Catalysis Society of Metropolitan New York 2024 Annual Spring Symposium



**Agile Strategy Lab – Central King Building
New Jersey Institute of Technology
Newark, New Jersey
Wednesday March 13th, 2024**

Acknowledgements

The Catalysis Society of Metropolitan New York gratefully acknowledges the following sponsors:



2024 Annual Symposium

The Catalysis Society of Metropolitan New York
 Wednesday, March 13th, 2024

8:00 AM	Registration (Coffee/Tea available)
8:40 AM	Opening Remarks Dr. Jihad Dakka <i>Chair</i>
8:45 AM	Welcoming Address <i>New Jersey Institute of Technology</i>
Session I Chair: Dr. Jihad Dakka	
8:50 AM	Keynote Address – Zeolite Catalysts for Light Alkane Dehydrogenation Dr. Raul Lobo <i>University of Delaware</i>
9:40 AM	Accelerating decarbonization by representing catalysts with natural language Dr. Marc Porosoff <i>University of Rochester</i>
10:10 AM	Opportunities for Fluid Catalytic Cracking in the transition towards a circular carbon economy Dr. Lucas Dorazio <i>BASF</i>
10:40 AM	Coffee Break
Session II Chair: Dr. Michele Sarazen	
11:00 AM	Identifying Mechanism & Kinetics of Electrochemical Hydrogenation & Hydrogenolysis of Furfural & Side Reactions in Acidic Electrolytes on Copper Dr. Elizabeth Biddinger <i>The City College of New York</i>
11:30 AM	A new mesoporous carbon catalyst carrier for flow applications Dr. Al Metauro <i>Exacer Catalyst Support</i>
12:00 PM	Descriptor Search for Metal Oxide Reactivity and Transport Dr. Randall Meyer <i>ExxonMobil</i>
12:30 PM	Lunch Break
1:20 PM	Poster Session
Session III Chair: Dr. Marco Castaldi	
2:45 PM	Tuning molecular interactions at catalytic surfaces to create tailored, local solvation environments for liquid phase reaction sequences Dr. Theodore Walker <i>Syracuse University</i>

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3:15 PM	Electrified Membrane Filtration for Active, Selective, Stable, and Low-Cost Nitrate Reduction Dr. Lea R. Winter <i>Yale University</i>
3:45 PM	Quantum Mechanical Insights into Light-Driven Reactions on Metallic Nanoparticles Dr. Mark Martirez <i>Princeton Plasma Physics Laboratory</i>
4:15 PM	Dynamic In Situ Spectroscopic Studies of TS-1 Catalyzed Epoxidation of Propylene Dr. Ive Hermans <i>University of Wisconsin Madison</i>
4:55 PM	Poster Awards
5:00 PM	Closing Remarks
5:05 PM	Adjourn

Poster Presentations

#	Presenter	Abstract Title	Affiliation
1	Chas Fields	Intensification of 4,4'-Dimethylbiphenyl Synthesis for Recyclable Diesters	University of Delaware
2	Cole Hullfish	Encapsulation of Au and Pd Metal in Zeolites for Oxidation Catalysis	Princeton University
3	Dang Nguyen	Oxidative Dehydrogenation of Ethane (ODHE) to Ethylene by the Bulk MoVNbTe (M1 Phase) Mixed Oxide Catalyst: Surface and Bulk Properties	Lehigh University
4	Diana García-Pérez	Pt supported on W-modified alumina and zirconia for <i>n</i> -dodecane hydroisomerization reaction	University of Delaware
5	Eli Ream	Direct Conversion of Ethylene to Propylene through Simultaneous Ethylene Dimerization and Olefin Metathesis with 8%NiSO ₄ /8%ReO ₄ /γ-Al ₂ O ₃ Catalyst	Lehigh University
6	Erin Sobchinsky	Ethylene Dimerization to n-butene with Nickel Sulfate on Zirconia: Investigation of the Molecular Structure and Activity of Surface Nickel and Sulfate Species	Lehigh University
7	Haider Ejaz	Phenol Hydrodeoxygenation over Ru(0001) surface, DFT and microkinetic modelling investigation with oxygen coverage effects	Rutgers University
8	Henry X. Jin	Ethylene Glycol Production on Transition Metal Phosphides from CO ₂ by Electrolysis: A Carbon-Negative Path to Sustainable Plastics	Rutgers University
9	James Trettin	Mechanistic Insights into Plasma-Assisted Catalysis by Operando DRIFTS	Princeton University
10	Jingzhi Liu	Impact of Support Hydrophobicity on Methane Catalytic Combustion over High-Silica Pd/CHA Zeolites under Lean-Burn Conditions	Syracuse University
11	Jinwoong Nam	Predicting Enthalpy of Hydrocarbon Radicals Adsorbed on Pt(111) Using Molecular Fingerprints and Machine Learning	Rutgers University
12	Kaitlyn Lawrence	Nitrogen oxide mitigation via a waste-derived heterogeneous mixed metal oxide	The City College of New York
13	Kathan Shukla	First Principles Investigation of Competing Aqueous Species on Nitrate Reduction to Ammonia on Cu-based Nanoparticles	New Jersey Institute of Technology
14	Mo Li	Enhancement of CO ₂ Reduction Reaction on Two Dimensional Catalysts Supported by a Ferroelectric In ₂ Se ₃ Substrate	New Jersey Institute of Technology
15	Moses D. Chilunda	Insights on the mechanistic understanding of the electrochemical reduction of furfural at the electrode-electrolyte interface	The City College of New York
16	Neelesh Kumar	Spectroscopic Elucidation of Phase Evolution in NiO/YSZ and LaFe _{0.9} Ni _{0.1} O ₃ under Oxidative and Reductive Gas Environments	Lehigh University

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17	Niladri Talukder	Physicochemical Changes for ORR Electrocatalysis Enhancement During Nitrogen-doped Graphene with Metal-organic Framework (N-G/MOF) Nanocatalyst Synthesis	New Jersey Institute of Technology
18	Rachel A. Yang	Kinetic ramifications of metal coordination and solvent environments for alkene oxidation over Fe and Cr carboxylate metal-organic frameworks	Princeton University
19	Samuel Moore	Understanding reactivity and structural impacts of contrasting earth-abundant metal-organic frameworks in the context of aqueous pollutant oxidation	Princeton University
20	Sayantani Sikder	Transient kinetics infrared reflection absorption spectroscopy studies of NO on Pd(111)	Stony Brook University
21	Shubham Gupta	Transition Metal Pnictides: Bioinspired Electrocatalysts for Converting CO ₂ to Multi- carbon Products from Scratch	Rutgers University
22	Sonia Arumuganainar	Design of ordered mesoporous oxides for dielectric barrier discharge-assisted catalysis of ammonia synthesis	Princeton University
23	Tianhao Hu	Active Site Identification, CO Oxidation, and Non-Thermal Plasma Reduction of Catalytic MOF Nanofilms	Stony Brook University
24	Weixin Li	Studies on the Synthesis, Reactivity, and Stability of Au Nanoparticles in Ti-MFI Zeolites for Propylene Epoxidation within H ₂ /O ₂ Mixtures	Syracuse University
25	Briana Espinosa, Anthony Ionta	Investigating key parameters for polynitrogen synthesis	New Jersey Institute of Technology
26	Yifei Li	Electrocatalytic CO ₂ Reduction on Single Crystal NiP ₂ Facets: Surface Intermediates and Mechanism Revealed	Rutgers University
27	Yue Qi	Catalytic Selective Hydrogenation of Aromatic Hydrocarbons to Cycloolefins	Stevens Institute of Technology
28	Adhika Setiawan	Microkinetic Modeling-driven Density Functional Theory Exploration of Ethylene Epoxidation on Partially Oxidized Silver Catalyst Surfaces	Lehigh University
29	Aojie Li	Elucidating the essential role of hydrogen bonding and direct H-transfer in transfer hydrogenation on transition metal catalysts	Lehigh University
30	Johari Dramiga	Thermodynamic and Kinetic Investigation of S Impurities in Solid Oxide Electrolysis Cell Feed Flow	Lehigh University

Oral Presentations

Keynote Address:
Zeolite Catalysts for Light Alkane Dehydrogenation

Raul F. Lobo

Center for Catalytic Science and Technology, Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716

The chemical industry is an important contributor of greenhouse gas emissions to the atmosphere and one of the goals of my research program is to develop process alternatives that can deliver the chemical products our modern society needs while minimizing CO₂ emissions. In this talk I will describe recent research on three classes of zeolite catalysts for light alkane dehydrogenation:

1. *Gallium- and zinc-containing zeolites*: We have investigated several zeolite structures (MFI, CHA and SZR), Si/Al ratios, and metal loadings and characterization techniques. This talk will summarize the salient findings of these investigations, in particular, the speciation of these metals in the zeolite pores, and the relation of these sites with catalytic rates of dehydrogenation.
2. *Mn-oxide supported on zeolite crystals*: We discovered that Mn-containing zeolites prepared by incipient wetness impregnation (IWI) catalyze the ethane dehydrogenation reaction with high selectivity. Preparation by IWI leads to the formation of Mn₂O₃ nanoparticles on the external surface of the zeolite crystals and these are the location of the active sites for both ethane and propane dehydrogenation. We will compare the effect of zeolite structure and composition on catalytic activity and stability.
3. *Oxidative Ethane Dehydrogenation over Zeolites*: B-chabazites (B-CHA) are excellent catalysts for the ODHE reaction, showing fast catalytic rates, with high selectivity towards ethylene from 500 to 600 °C. The zeolite pores stabilize surface B species leading to a negligible decrease of boron content in the spent B-CHA catalyst. A reaction network and a model for the active sites based on 11B NMR spectroscopy are proposed.

Accelerating decarbonization by representing catalysts with natural language

Marc Porosoff

Department of Chemical Engineering, University of Rochester, Rochester, NY 14627

Accelerating deployment of decarbonization technologies is desperately needed to limit global warming to less than 2 °C. The petrochemical industry is particularly difficult to decarbonize because the CO₂ intensive thermocatalytic processes are entrenched in our infrastructure. To enable rapid decarbonization, we are redefining catalyst representation and structure-property relationships with large language models (LLMs). The result is a new research direction where we represent catalysts by the synthesis method, reaction conditions, and performance. The method is therefore verifiable and actionable – we can immediately synthesize and test the outcomes generated by the model. The objective of this work is demonstrating that natural language processing will accelerate catalyst discovery because the rate determining step of catalyst characterization is not needed for accurate representation.

Our proposed methodology accelerates catalyst predictions with natural language processing and Bayesian optimization (BO), while leveraging practical knowledge to reduce the size of the experimental space. We focus our initial efforts on developing and understanding trimetallic catalysts for the reverse water-gas shift (RWGS) reaction. We are motivated by the philosophy that the catalysts we study must be earth-abundant, low-cost, and scalable for rapid implementation to accelerate decarbonization. We are focusing on trimetallic catalysts because they are more difficult to characterize than bimetallics, making them a good fit for an approach that does not need the catalyst structure to be predictive. Furthermore, the number of possible trimetallic catalysts is orders of magnitude larger than that of the bimetallics, an important consideration when searching for a novel catalyst. To build-up the fundamental understanding of our approach, we are focusing our efforts on addressing the following questions: (1) How do we design the experimental space to rapidly identify novel, active, selective, and stable RWGS catalysts? (2) Is our method overly sensitive to experimental artifacts and irreproducible results? (3) What mechanistic information can we learn from representing catalysts with language?

Opportunities for Fluid Catalytic Cracking in the transition towards a circular carbon economy

Lucas Dorazio

BASF Corporation, 25 Middlesex Essex Turnpike, Iselin, NJ 08830 (USA)

The integration of recycled and renewable waste streams into chemical value chains is a challenging topic being driven by the need to make circularity in the production of chemicals and fuels a reality. Increased circularity in manufacturing will come from the combination of both chemical recycling of fossil carbon and insertion of renewable carbon into refined products. The use of existing refinery processes for upgrading renewable and recycled feedstocks will offer the opportunity to reduce implementation cost and allow for a gradual transition from conventional oils. The properties of recycled and renewable feedstocks will vary considerably and, in some cases, depart significantly from the properties of conventional oils making some feedstocks more challenging to integrate into existing refinery assets than others. One process available to refiners is Fluid Catalytic Cracking (FCC) that has proven to be a valuable refinery process for converting low value fractions of conventional oil into high value products. The ability of the FCC process to manage metal contaminants, manage catalyst deactivation, and tolerate a wide variety of feedstocks will likely prove to be valuable once again for these new feedstocks, particularly for the more challenging oxygenated feedstocks not suitable for other refinery processes. As the chemical industry transitions towards a circular carbon economy, the FCC unit has the potential to remain a vital refinery asset in the future. As one of the leading suppliers of commercial FCC catalyst, BASF is actively exploring the chemistry associated with these different feedstocks and the implications it will have on refinery processes and needs for new catalytic materials to enable refiners to achieve their sustainability targets. In this contribution, opportunities for catalytic cracking and the FCC process for the upgrading of renewable and recycled feedstocks will be discussed. Additionally, how feedstock chemistry influences product yields during catalytic cracking, how the design of the catalyst can be used to direct product yields, and what dictates the need for additional hydrogen be introduced through co-processing with other feedstocks will be presented.

Identifying Mechanism & Kinetics of Electrochemical Hydrogenation & Hydrogenolysis of Furfural & Side Reactions in Acidic Electrolytes on Copper

Elizabeth J. Biddinger, PhD

Department of Chemical Engineering, The City College of New York, CUNY

Electrochemical synthesis methods offer opportunities to perform reactions under benign reaction conditions (at or near room temperature and pressure), use less harmful or waste-generating reaction steps, perform selective reactions and utilize renewable electricity directly. In electroreduction reactions, externally-supplied hydrogen gas that is generally needed for reduction is not required. Instead, electrons and the electrolyte can serve as the sources for the reducing agents. Pairing renewable-electricity driven processes with renewable feedstocks such as biomass has the opportunity to further increase the sustainability of reactions. Furfural, a biomass-derived feedstock that is commercially produced at ~400,000 tons/year, can be reduced using electrochemical hydrogenation and hydrogenolysis (ECH) into furfuryl alcohol and 2-methyl furan over copper in acidic electrolytes. The ECH reactions also compete with hydrogen evolution and acid-derived side products in the reactor. By tuning the reaction conditions, the desired products can be formed and undesired products minimized. Utilizing traditional heterogeneous catalysis techniques, the kinetics of the ECH reactions and competing side reactions can be determined. The source of the fouling and its potential dependence can also be identified. The kinetics and reactor operation details can be combined into an overall mass balance that enables better understanding of the system and identify opportunities for further improvement.

A new mesoporous carbon catalyst carrier for flow applications

M. M. Schubert^{1*}, A. Metauro², M. Baraldi¹

¹Exacer SRL, via Puglia 2/4, 41049 Sassuolo, IT

²Novita Technology LLC, Hillsborough, NJ 08844 USA

Introduction

There are two clear trends that drive the need for dedicated carbon carriers for fixed bed application: one area is in pharmaceutical and other fine chemical processes such as aroma chemicals. There is a strong desire to convert slurry beds to flow chemistry, which, as a continuous process, is much more efficient and helps to prevent metal losses which occur in the filtering step of slurry processes. Secondly, there is currently a huge variety of new ‘sustainable’ processes coming up, such as waste recycling, deriving chemicals from biomass-based raw materials and the production and transport of hydrogen. In common, the processes typically contain a huge portion of water and therefore often are carried out under hydrothermal conditions and sometimes even at extreme pH-values, where standard carriers, such as alumina, silica or even zirconia are no longer a viable option.

There are already some examples of carbon carriers on the market, but they either lack in purity and mechanical stability and often have only micropores, which induces diffusion issues, or they are in a price range, that is prohibitive for most applications.

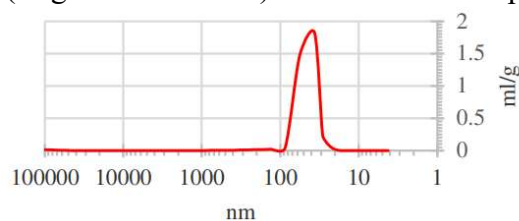
Materials and Methods

Exacer presents a new class of carbon carriers, which are almost purely mesoporous, and which show comparable mechanical features, for example to gamma-alumina extrudates, which are used routinely in fixed bed applications. The new carriers also remain fully stable under hydrothermal conditions at any pH value. The carbon material is already produced at tonscale and has an industrial application in processes for sugar-based chemicals.

Table 1. Typical physical properties of the new carbon carrier.

Dimensions	Extruded Cylinder Ø1.5 mm
BET	~200 m ² /g
Hg Pore Volume	~0.8 ml/g
Micropore Volume	<0.05 ml/g
Crush Strength	30 N
Loss on attrition (ASTM D4058)	~1%

Figure 1. Hg Pore Volume (Log Diff. Intrusion) for new carbon support.

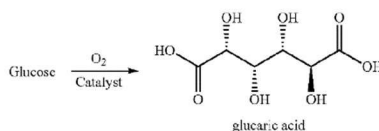


A Pt/Au-catalyst (0.8% Au, 1.2% Pt) on carbon was prepared using the new carbon support as well as on other commercially available activated carbon extrudates for comparison purposes. Details on the catalyst preparation are available from ref.1.

20 g of catalyst were placed into a reactor with a diameter of 1.3 cm and an effective bed length of ~60 cm. The reaction was carried out at 130°C and 750 psi. The liquid flow was 2 ml/min, and the gas flow 768 ml/min. More details are provided in ref. 1.

Results and Discussion

The different Pt-Au/Carbon catalysts were tested for the catalytic oxidation of glucose to glucaric acid¹:



The new carbon carrier clearly gave the best yields and selectivity, when compared to the reference samples.

Table 2. Yields and Selectivity for various Pt-Au/Carbon catalysts for the catalytic oxidation of glucose to glucaric acid.¹

Carrier type	Yield	Selectivity
New carbon carrier	52%	87%
Donau Supersorbon K4-35	22%	66%
Donau Supersorbon SX30	18%	68%
Norit RX3 Extra	20%	70%

Significance

A new carbon carrier is presented, that has outstanding mechanical features, which allow for a use in fixed bed applications. This and its mesoporous pore structure makes it predestined for the conversion of larger molecules, particularly under hydrothermal conditions.

References

1. US 10,654,027 B2

Descriptor Search for Metal Oxide Reactivity and Transport

Randall Meyer¹, Sumathy Raman¹, Daniele Vivona², Kiarash Gordiz², Yang Shao-Horn², Hansel Montalvo³ and David Hibbitts³

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Metal oxides play a prominent role in enabling many important technologies such as heterogeneous oxidation catalysis, oxygen transport membranes, solid oxide fuels and oxygen storage materials. In the Inorganic Crystal Structure database nearly 40,000 pristine oxide structures have been recorded. However, when dopants to the crystal lattice are considered, the number of different synthesizable metal oxide materials grows even further. Descriptors for their reactivity and ion conductance that capture the effect of local structure are therefore highly desirable in order to focus researchers on the most appropriate set of materials for a given application. Different classes of descriptors for oxygen ion transport have been identified which account for the geometric effects (e.g. void volume, transport window), electronic structure effects (e.g. M-O bond strength) and dynamic effects (e.g. phonon band center). Similar descriptors have previously been developed for reactivity of metal oxide surfaces. In this work, building upon the previous literature, we hope to develop multi-descriptor predictive relationships as no single descriptor can capture the complex chemistry of these materials. In addition, we attempt to build descriptors based on local structure as bulk material properties may not be reflective of the atomistic level events described here in transport and catalysis. Although we focus here primarily on oxygen ion transport, some implications and approaches for the more complicated problem of surface reactivity will be presented.

Tuning molecular interactions at catalytic surfaces to create tailored, local solvation environments for liquid phase reaction sequences

Theodore Walker

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A key challenge in the design of new catalyst formulations is elucidating those factors which control the activity, selectivity, and stability of catalytic materials; and leveraging these insights to synthesize materials with desirable properties. In this work, we present initial attempts to design and synthesize a series of materials comprising supported metal and acid catalysts decorated with polymer brushes – i.e., polymer moieties of well-defined composition and dimensions grafted directly onto supports, proximal to active sites. Through non-bonding interactions with solvated reactant molecules, the polymer brushes create tailored local solvation environments so that select reactant states are stabilized over others. As a proof of concept, we demonstrate how a polyimide-modified WO_3/SiO_2 catalyst enhances the selectivity of fructose dehydration to 5-hydroxymethylfurfural (HMF) by suppressing the rate of side reactions relative to the rate of HMF production. To interrogate this behavior, we propose to use molecular dynamics (MD) simulations to estimate the solvation free energy change associated with transferring fructose and 5-hydroxymethyl furfural from the bulk solvent into the local solvation environment of the polymer brushes, modulating their length, composition and grafting density in the MD simulations, and quantifying the preferences of the solvated reactants and products for the polymer brushes versus the bulk liquid phase as a function of same. Those polymer-modified catalyst systems that, based upon our solvation free energy calculations, are anticipated to maximize selectivity to HMF will be synthesized, and tested in bench-scale glass batch reactors. This work represents a new direction in heterogeneous catalyst research: modification of solid catalysts with polymer moieties to tune weak interactions in the liquid phase, and therefore control reactivity and selectivity in liquid-phase reactions.

Electrified Membrane Filtration for Active, Selective, Stable, and Low-Cost Nitrate Reduction

Lea R. Winter

Chemical and Environmental Engineering, Yale University, New Haven, CT 06520

The release of nitrate to the environment from wastewater effluent and agricultural runoff contributes to groundwater contamination, harmful algal blooms, and disruption of biogeochemical nitrogen flows. Nitrate conversion via electrochemical reduction can eliminate the production of concentrated waste streams by generating either harmless (N_2) or useful (NH_3) products. However, major challenges for nitrate removal from water via electrochemical conversion involve reducing the use of expensive precious metal electrocatalysts while also improving the reaction activity, selectivity, stability, and mass transport of nitrate to electrocatalyst active sites.

We have developed nanoporous electrified membranes (EMs) as flow-through electrodes to achieve active, selective, stable, and nitrate reduction using earth-abundant materials. The EMs show significantly higher nitrate removal activity during electrified filtration compared to flow-by mode. The small pore sizes in the membrane reduce the diffusional boundary layer by several orders of magnitude with respect to flow-by mode, overcoming diffusional mass transport limitations. These advantages enable use of metal-free carbon nanotube-based EMs to achieve nitrate removal to below EPA drinking water limits in synthetic and real surface water, with product selectivity to N_2 of over 80% and stability over more than 100 h. By controlling selective separation properties in the membrane, we can also modify the reaction selectivity to enable energy-efficient ammonia synthesis from low concentration nitrate. The precious metal-free, mechanically flexible membrane electrodes demonstrate a new strategy to drastically improve electrocatalytic performance without complex catalyst materials innovation, potentially providing practical and sustainable solutions for both water treatment and ammonia synthesis.

Quantum mechanical insights into light-driven reactions on metallic nanoparticles

John Mark P. Martirez

Princeton Plasma Physics Laboratory, Princeton University, New Jersey 08540

The nearly-free-electron-like valence electrons in some metallic nanoparticles (MNPs) facilitate their enhanced ability to scatter/absorb light by means of local surface plasmon resonances (LSPRs). When the incident light has a frequency resonant with the MNP's LSPR, amplified electric fields are generated within and surrounding the MNPs that can lead to hot charge-carrier generation, induce local heating, or cause excitations of molecules or other materials nearby. Photocatalysis mediated by MNPs exploits this unique optical phenomenon. First-principles quantum mechanics can aid in understanding such light-driven chemistry, but the methods used must properly account for both electronic excitations and surface reactions. We therefore used embedded correlated wavefunction (ECW) theory to simulate chemical reactions on metallic surfaces and calculate their ground- and excited-state energy curves. ECW calculations of a variety of reactions on pure and surface-doped metals reveal that enhanced kinetics can occur on excited-state reactive potential energy surfaces accessed *via* plasmon-enhanced light absorption or resonance energy transfer between the MNP and the surface-active site. Our calculations explain experimentally observed enhanced rates and, in some cases, modification of product selectivity, due to plasmon-driven electronic transitions.

Dynamic In Situ Spectroscopic Studies of TS-1 Catalyzed Epoxidation of Propylene

Ive Hermans

*UW-Madison, Department of Chemistry, Department of Chemical and Biological Engineering,
Wisconsin Energy Institute, Madison Wisconsin, USA*

Heterogeneous Ti-containing catalysts such as TS-1 and Ti-MWW are industrially used for the epoxidation of propylene-to-propylene oxide using H_2O_2 (HPPO). The TS-1 catalyst operates best in methanol as solvent but unfortunately this also leads to a number of undesired ring-opened by-products. Such by-products can be avoided by using acetonitrile as a solvent. However, TS-1 performs far less in this alternative solvent. Various feed-modifiers and promoters further boost the performance of this catalytic system, but we lack molecular understanding of the mechanisms. In my talk I will describe the use of IR Modulation Excitation Spectroscopy (MES) to gain unique insights in the interaction of the active sites with $\text{H}_2\text{O}_2/\text{H}_2\text{O}/\text{solvent}$. MES is a dynamic technique where the concentration of one of the reagents is periodically altered. By studying the response of the system to this perturbation we can filter out noise and signals stemming from spectator species and obtain kinetic insights in the activation and transformation of reagents at the liquid-solid interface.

Poster Presentations

Intensification of 4,4'-Dimethylbiphenyl Synthesis for Recyclable Diesters

Chas Fields, Dionisios G. Vlachos, and Raul F. Lobo*

Chemical and Biomolecular Engineering, University of Delaware, 150 Academy St., Newark, DE, 19716.

Reducing our dependence on petroleum-derived chemicals requires the development of renewable alternatives to replace these established products. Recent investigations demonstrated a pathway to prepare 4,4'-dimethylbiphenyl (DMBP), an attractive platform chemical for producing metal-organic frameworks, plasticizers, and polymers, from readily available biomass precursors. The synthesis of DMBP follows a two-step process: 2-methylfuran (MF) oxidatively couples to yield 5,5'-dimethyl-2,2'-bifuran (DMBF). DMBF then undergoes tandem Diels-Alder and dehydration with ethylene to afford the desired DMBP. Prior research identified conditions that achieved 63% MF conversion and 59% DMBF yield, leaving room for improvements in DMBP production. We researched process and catalyst alternatives to improve the productivity of this valuable molecule. A baseline DMBF space-time yield of 0.59 mol L⁻¹h⁻¹ was established via the reaction conditions initially reported. A surface response design identified an initial optimum at 44 °C and a MF/solvent molar ratio of 0.713, achieving a DMBF space-time yield of 0.75 mol L⁻¹h⁻¹. Temperature effects at the optimum MF/solvent ratio showed that as the reaction reaches complete conversion of MF, DMBF reacts to form undesired byproducts. For maximum productivity, the reaction time was reduced to 1.5 hours at a temperature of 67 °C affording a MF conversion of 96.2% and DMBF yield of 77.5% with a DMBF space-time yield of 1.10 mol L⁻¹h⁻¹, an 86.4% increase from the baseline. Scale-up efforts resulted in a 44x increase in DMBF production, bringing the process from milligrams to grams. For the second step, a homogenous Lewis acid catalyst in the Diels-Alder-Dehydration reaction demonstrated a 54.3% increase in DMBP yield at reduced temperatures compared to the initial protocols. Amplification of the Diels-Alder-Dehydration to a 3 g scale demonstrated large-scale feasibility while maintaining selectivity for the DMBP product. This positions renewable DMBP as an asset for reducing petroleum consumption.

Encapsulation of Au and Pd Metal in Zeolites for Oxidation Catalysis

Cole W. Hullfish and Michele L. Sarazen*

Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544

Methane partial oxidation (MPO) to methanol with subsequent methanol-to-hydrocarbons (MTH) is an enticing pathway for energy-efficient natural gas upgrading to liquid chemicals. Gold-palladium (AuPd) nanoparticles present as promising catalysts for MPO, as they are active for MPO by hydrogen peroxide (H_2O_2) and H_2O_2 synthesis from H_2 and O_2 . Encapsulation of AuPd metal within microporous zeolite frameworks is attractive for maximizing metal surface area, increasing catalyst thermal stability, and enabling tandem catalysis (MTH) on zeolitic acid sites, but requires development of synthesis strategies for AuPd encapsulation in a diverse range of zeolites. Here, encapsulated metal (Au, Pd, AuPd) in MFI and BEA are prepared via direct hydrothermal syntheses utilizing 3-mercaptopropyl trimethoxysilane to ligate metal precursors during zeolite crystallization. Powder X-ray diffraction indicates that zeolite-encapsulated metal nanoparticle catalysts are well-crystallized, and transmission electron microscopy reveals well-dispersed metal ($d_{TEM} = 1-3$ nm). Further, diffuse reflectance UV-vis suggests a prevalence of alloy AuPd nanoparticles, as the localized surface plasmon resonance band indicative of bulk gold (~ 500 nm) is absent from their spectra. Encapsulation efficiencies were measured through oxidation rates of small alcohols relative to bulky alcohols that cannot access zeolitic micropores as well as small alcohol oxidation in the presence of bulky titrants, both methods revealing high ratios of intracrystalline to extracrystalline metal surface areas across metals (Au, Pd, AuPd) and zeolite frameworks (MFI, BEA). Insights from these tailored catalyst syntheses can be applied to other metals and zeolite frameworks for more precise syntheses of thermally stable bifunctional catalysts.

Oxidative Dehydrogenation of Ethane (ODHE) to Ethylene by the Bulk MoVNbTe (M1 Phase) Mixed Oxide Catalyst: Surface and Bulk Properties

Dang D. Nguyen¹, Bar Mosevitzky Lis^{1,2}, Rebecca Fushimi³, Israel E. Wachs^{1,*}

¹*Operando Molecular Spectroscopy and Catalysis Research Lab, Department of Chemical & Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, USA*

²*Department of Chemical Sciences, University of Limerick, Limerick, Ireland*

³*Idaho National Laboratory, Idaho Falls, ID 83415, USA*

Oxidative dehydrogenation of ethane (ODHE) to ethylene is an alternative method to circumvent thermodynamic limitation, coke formation, and greenhouse gas emissions associated with conventional steam cracking of ethane to produce ethylene. Recently, the bulk M1 phase of the crystalline MoVNbTe mixed oxide catalyst has gained popularity over other types of ODHE catalysts due to its high ethylene selectivity (> 90%) and good ethane conversion (up to 65%). In the present study, bulk-sensitive (Raman) and surface-sensitive (in situ High Sensitivity-Low Energy Ion Scattering (HS-LEIS)) techniques are employed to characterize the MoVNbTe mixed oxide catalyst.

Pt supported on W-modified alumina and zirconia for *n*-dodecane hydroisomerization reaction

Diana García-Pérez, Gema Blanco-Brieva, M. Consuelo Alvarez-Galvan, and Jose M. Campos-Martin

Instituto de Catálisis y Petroleoquímica. Calle Marie Curie 2, 28049-Madrid, España.

The use of green fuels is an interesting alternative towards the transition to clean and renewable energy. These fuels can be obtained from biomass residues and drop-in in the current infrastructure, transport, and storage. The use of this green fuels reduces the CO₂ emissions and employes residues in a circular economy. Furthermore, the use of green fuels will play a critical role in the decarbonization of the economy in some niches which are difficult to be electrified in medium term. Among them, the use of sustainable aviation fuels is essential for the decarbonization of air transport. Hydrotreatment of vegetal oils (HVO) is an interesting process to reach this goal.

The present work is related with the second step of HVO process, which is the hydroisomerization (HISO) reaction. In the hydroisomerization step, the mixture of lineal hydrocarbons is converted in branched hydrocarbons and this new mixture has exceptional properties as fuel. Considering the results published in the literature for long chain paraffin hydroisomerization and our previous study on the influence of the reduction temperature and nature of the support on hydroisomerization, this work aims to study the influence of W loading, preparation method and nature of the support during the hydroisomerization of *n*-dodecane in order to improve the quality of linear alkane fuels obtained by HVO or Fischer-Tropsch synthesis, producing a suitable fuel.

Thus, in this study, the hydroisomerization of *n*-dodecane is mainly discussed with respect to the use of bifunctional catalysts with different W loadings (3-18 wt. % W). Pt supported (0.3 wt.% Pt) on W-modified alumina and zirconia were used as the catalysts.

Direct Conversion of Ethylene to Propylene Through Simultaneous Ethylene Dimerization and Olefin Metathesis with Dual-Site Supported 8%NiSO₄/8%ReO₄/γ-Al₂O₃ Catalyst

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The direct conversion of ethylene to propylene (ETP) through simultaneous ethylene dimerization and olefin metathesis is a promising method for propylene production that is currently in development. In ethylene dimerization, ethylene reacts to form butenes, and in olefin metathesis, ethylene and 2-butene react to form propylene. Ethylene dimerization catalysts are typically Ni-based and olefin metathesis catalysts are typically Mo-, W-, or Re-based. In this study, a supported 8%NiSO₄/8%ReO₄/γ-Al₂O₃ dual-site catalyst was synthesized for the direct conversion of ethylene to propylene, in which NiSO₄ performs ethylene dimerization to butenes (primarily 2-butene) and ReO₄ performs olefin metathesis of ethylene and 2-butene to propylene. The supported 8%NiSO₄/8%ReO₄/γ-Al₂O₃ catalyst was extensively physically characterized at the molecular-level (in situ Raman, IR spectroscopy, UV-vis spectroscopy, X-ray absorption spectroscopy, High Sensitivity-Low Energy Ion Scattering (HS-LEIS)) and chemically probed (C₂=-TPSR, C₃=-TPSR, and steady state ethylene dimerization and olefin metathesis reactions). The physical characterization studies revealed that rhenia and sulfate are present as surface (O=)2ReO₂ and O=SO₃ sites on the alumina support. The nickel oxide was primarily present as NiO₆ sites that are distributed between the surface and alumina bulk lattice. The individual surface SO₄ and NiO₆ sites did not perform ethylene dimerization and only performed ethylene dimerization when they were both present suggesting a synergistic interaction between them. Neither of the surface SO₄ and NiO₆ sites performed olefin metathesis. The surface ReO₄ sites only performed olefin metathesis. Addition of surface ReO₄ to the NiSO₄/Al₂O₃ catalysts modestly enhanced the rate of ethylene dimerization and addition of NiSO₄ to ReO₄/Al₂O₃ significantly enhanced the rate of olefin metathesis. These promotional activity changes are related to competitive adsorption of these oxides on specific surface hydroxyls of the alumina support. These results provide new insights about the structure-function relationship of the dual site supported 8%NiSO₄/8%ReO₄/γ-Al₂O₃ catalyst for direct conversion of ethylene to propylene.

**Ethylene Dimerization to n-butene with Nickel Sulfate on Zirconia:
Investigation of the Molecular Structure and Activity of Surface Nickel and
Sulfate Species**

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Due to the growing abundance of shale gas, industry has shifted to processing lighter hydrocarbon feedstocks which has contributed to a decrease in the production of butene. This has stimulated interest in the dimerization of shale gas derived ethylene to butene. In industry, ethylene dimerization is carried out in homogeneous systems which can face several operational and environmental challenges. Consequently, there is interest in developing heterogeneous ethylene dimerization catalysts with comparable performance to their homogeneous counterparts. Nickel sulfated zirconia is a promising heterogeneous ethylene dimerization catalyst due to its high activity and selectivity for 2-butene under mild reaction conditions as well as its high surface acidity and well dispersed nickel phase. However, little is known about the nature of the sulfate and nickel sites as well as the structure-activity relationships that are responsible for ethylene dimerization activity. To address these gaps in the literature, this work focuses on determining the nature of the surface structures and the interactions between the nickel and sulfate species that increase the dimerization activity and butene selectivity. Several characterization techniques (in situ IR, Raman, and UV-vis spectroscopy, ethylene-TPSR, in-situ XAS and LEIS) were applied under different environments. Dehydrated IR and Raman spectra indicated the presence of O=S(O-Zr)₃ sulfate species which preferentially anchor to terminal hydroxyls on the zirconia support at low loadings. At high loadings, a second sulfate species anchors to the tri-bridging hydroxyls. XAS and UV-vis spectra collected under dehydrated conditions indicated that nickel is present as Ni²⁺O₆ while spectra collected during ethylene dimerization indicated that these sites are stable during reaction. Ethylene-TPSR also demonstrated that both nickel and sulfate are necessary for ethylene dimerization activity. IR spectra of adsorbed NH₃ also revealed that the order of impregnation of nickel and sulfate alters the Bronsted to Lewis acid ratio and temperature for butene formation.

Phenol Hydrodeoxygenation over Ru(0001) surface, DFT and microkinetic modelling investigation with oxygen coverage effects

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Bio-oil produced from fast pyrolysis of biomass feedstock contains oxygenated compounds and requires upgrading through hydrodeoxygenation (HDO) under high pressure (200 bar) and temperature (200° to 400°C) conditions to improve fuel quality and energy content. Model species like phenol and guaiacol are studied to elucidate the mechanics of HDO over catalytic surfaces. Among metallic catalysts, ruthenium is selective towards deoxygenated products. A detailed study of the mechanisms of HDO of phenol over Ru(0001) surface was carried out to identify the energetically favorable pathways towards desirable products including Cyclohexanol, Cyclohexane, Cyclohexanone and Benzene. Three mechanisms were investigated which differ based on when deoxygenation takes place and were compared based on key reactions. This energetic comparison is followed by a kinetic analysis which involved vibrational frequency calculations for elementary reactions for all mechanisms studied. The microkinetic model based on the identified pathways can provide qualitative comparison between the experimental results and our computational analysis showing that the calculated product preference agrees with the experimental results. The kinetic model further indicates oxygen coverage over the metal surface to increase, thus changing the catalytic environment. The change in product preference is studied with increased oxygen coverage of the Ru(0001) surface to achieve a better quantitative comparison with experiments. The microkinetic model predicts high oxygen coverage at operational temperatures for a clean Ru(0001) surface. Oxygen removal from phenol occurs prior to ring hydrogenation even though the energetics are unfavorable for this outcome resulting in a high benzene production. The oxygen that is removed from phenol stays on the surface with its removal in the form of water being unfavorable. We observe increasing unfavourability of deoxygenation over an oxygen covered surface which is key to increasing oxygenated product formation. Deoxygenation energetics become markedly unfavorable around a quarter oxygen monolayer formation. This insight helps improve the microkinetic model which shows lower oxygen coverage as deoxygenation becomes unfavorable.

Ethylene Glycol Production on Transition Metal Phosphides from CO₂ by Electrolysis: A Carbon-Negative Path to Sustainable Plastics

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Among the transition metal phosphides (TMPs), nickel phosphide compounds (Ni₂P) are the most energy efficient electrocatalysts that can produce complex multi-carbon products (C₁ to C₄) from carbon dioxide, although controlling C-product selectivity remains challenging. We recently reported that a significant improvement in product selectivity to ethylene glycol (83%) on Ni₂P can be achieved by use of a Lewis acid/base co-catalyst to control the branching between C-C coupling and hydride reduction. (Li, 2024, EES Catalysis) Our current work now demonstrates that controlling flux through this branchpoint can be achieved in a single electrocatalyst without the addition of a Lewis acid/base co-catalyst. We observe that MoP₂ acts as an electrocatalyst for the production of ethylene glycol and 2,3-furandiols via ethylene oxide as an intermediate. Of note, ethylene glycol has a global production volume of over 60 million tons per year. It is commercially derived through emission-intensive hydrolysis of ethylene oxide made from petrochemically sourced ethylene. Through the tuning of reaction conditions, including electrolyte concentration and applied potential, this project examines how to optimize production of this high-demand chemical, while contributing to the greater understanding of carbon dioxide reduction mechanisms on TMP catalysts. From this study, we have learned that replacing Ni with Mo changes the mechanism of C-C bond formation from aldol condensation to direct dimerization (C₂ to C₄), thus bypassing C₃ intermediates. Further mechanistic work on MoP₂ and other TMP electrocatalysts has the potential to produce carbon-negative chemicals by design from scratch. Supported by a DOE-STTR contract.

Mechanistic Insights into Plasma-Assisted Catalysis by Operando DRIFTS

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Given the critical need to limit our dependence on fossil fuels for energy and chemicals, it is vital to engineer chemical reactions that sustainably produce platform molecules using renewable electricity to limit greenhouse gas (GHG) emissions. One such reaction is the dry reforming of methane (DRM) that converts methane and carbon dioxide (both GHGs) into syngas, which is a mixture of carbon monoxide and hydrogen that is valuable for upgrading to higher order hydrocarbons and liquid oxygenates via Fischer-Tropsch chemistry. While thermal DRM is limited by the activation of thermodynamically stable methane and by catalyst deactivation from adsorbed carbonaceous species, we propose an electrified plasma-assisted catalytic approach, a direct electron process that activates methane and carbon dioxide near ambient temperature and pressure. While plasma alone can activate these molecules, it is often unselective, requiring a catalyst to tailor the selectivity to desired products. Furthermore, plasma-assisted catalysis has been shown to benefit from a synergistic effect due to the interactions of the plasma discharge on the catalyst and vice versa. One primary challenge facing effective catalyst design for plasma-assisted catalysis is a lack of fundamental understanding of plasma/catalyst interactions during reaction. In this work, we demonstrate the use of a dielectric barrier discharge (DBD) plasma jet interfaced with a diffuse reflectance (DR) reaction chamber for operando DR infrared Fourier transform spectroscopy (DRIFTS). We study the plasma-assisted oxidation of carbon monoxide on Pt/Al₂O₃ as a suitable probe reaction for evaluating the strengths and limitations of the jet/cell configuration for mechanistic studies of plasma/catalyst interactions. Our work here has revealed the ability for certain plasma discharges to oxidize the active metal catalyst and to alter active metal nanoparticle restructuring mechanisms, which has significant impacts on reaction rates.

Impact of Support Hydrophobicity on Methane Catalytic Combustion over High-Silica Pd/CHA Zeolites under Lean-Burn Conditions

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Methane, while being the primary component of natural gas and a significant energy source, possesses a global warming potential more than 80 times greater than CO₂ over a 20 year span. Thus, complete catalytic oxidation of CH₄ into CO₂ is considered to be an effective strategy for minimizing the environmental impact of CH₄ emissions, while producing lower levels of NO_x than conventional thermal combustion. Although Pd/Al₂O₃ and Pd/ZrO₂ catalysts are active for CH₄ oxidation at stoichiometric conditions, they fail to maintain adequate CH₄ conversion and stability under lean-burn conditions at low temperatures in the presence of various combustion products such as H₂O and SO₂. By contrast, Pd-containing zeolites with high Si/Al molar ratios, such as Pd/SSZ-13 (CHA), have shown superior performance in achieving complete CH₄ oxidation even in the presence of H₂O and remain hydrothermally stable due to their hydrophobicity and superior hydrothermal durability. 1 wt.% Pd/CHA (Si/Al = 15-137) were synthesized in both OH and F media and evaluated for CH₄ oxidation performance before and after simulated aging at 650 °C for 1 hour under wet-lean conditions. When comparing the temperatures required to achieve 50% and 90% CH₄ conversion, it was observed that CH₄ oxidation performance improves with increasing hydrophobicity and Pd/CHA catalysts (Si/Al > 33) exhibited superior performance compared to Pd/Al₂O₃. At 250 °C, the steady-state CH₄ oxidation rates on 1 wt.% Pd/CHA-F-80 under wet-lean condition were 9.5×10^{-9} moles CH₄ gcat⁻¹ s⁻¹, or $\sim 2.3 \times$ greater than Pd/Al₂O₃. The study of H₂O order and activation barrier indicates a weaker H₂O inhibition effect and a lower activation barrier on Pd/CHA catalysts compared to Pd/Al₂O₃. The results demonstrate that, for Pd/CHA catalysts, increasing Si/Al ratios, i.e., hydrophobicity, or changing the synthesis media to F media, can improve the catalyst stability and reduce the inhibition effect on CH₄ oxidation rate.

**Predicting Enthalpy of Hydrocarbon Radicals Adsorbed on Pt(111) Using
Molecular Fingerprints and Machine Learning**

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The reliable prediction of properties for the adsorbates including their enthalpy has been a long-standing challenge as a first key step in studying surface reactions. It is especially difficult when large adsorbates are involved as the interactions between the adsorbates and surface atoms are complex. Here, we developed machine learning models for the prediction of the formation enthalpy of various C₂ to C₆ hydrocarbon adsorbates on Pt(111) surface based on 384 density functional theory calculations. Focusing on larger and more intricate adsorbates, two-thirds of the total species were C₆ species. Four molecular descriptors that represent the valency and bonding of individual carbons within the adsorbates were generated without intensive computation. They were subsequently used as the features of the machine learning models with three linear and four non-linear algorithms. The models were developed with 30 different samplings of train/test sets and their results were statistically analyzed to ensure the performance of the models. Non-linear models, especially kernel ridge regression and Extreme Gradient Boosting, outperformed linear models with lower absolute errors. The top two accurate models, based on these algorithms, also displayed remarkable robustness in predicting various species. Employing ensemble average voting with these two models, the lowest mean absolute error of 0.94 kcal/molC was achieved. Finally, machine learning was used to estimate the formation enthalpy of 3,115 hydrocarbon adsorbates on Pt(111) highlighting the promise of these methods to study more complicated reaction networks.

Nitrogen oxide mitigation via a waste-derived heterogeneous mixed metal oxide

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The solid residual, ash, of municipal solid waste (MSW) combustion is known to contain trace amounts of platinum group metals, rare earth elements, and other critical metals. Some of these metals are known to act as active sites in catalysts designed for the denitrification (deNO_x) processes, but to date, no publications detail the use of MSW-derived ashes as a stand-alone deNO_x catalyst. This work studies the activity of municipal solid waste (MSW) combustion ash in the reductive decomposition of nitric oxide. Four basic aspects were investigated: the role of oxygen in the treated gas in the catalytic performance, the equilibrium reactions responsible for observed temperature-dependent shifts in selectivity, how reductant choice impacts catalyst stability, and how pretreatment impacts performance. The presence of oxygen in the treated gas stream was shown to more than double NO conversions despite observing no change in oxygen consumption. An NO oxidation step is proposed as the mechanistic step responsible for the temperature-dependent, non-linear shift in selectivity. The presence of H₂O in the treated stream resulted in ash sintering, and thus a loss in surface area, whereas the use of other reductants such as H₂ and NH₃ did not modify ash surface area during performance testing. Reductive pretreatment of ash improved conversion of NO by as much as double, while oxidative pretreatment depressed conversion to as little as half the conversion of as-received ash.

First Principles Investigation of Competing Aqueous Species on Nitrate Reduction to Ammonia on Cu-based Nanoparticles

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Nitrate reduction to ammonia (NRA) is critical for environmental remediation and energy conservation, as it can remove harmful NO₃⁻ from water sources while producing useable NH₃. Copper (Cu) represents one of the most promising non-noble-metal NRA electrocatalysts. However, the intrinsic catalytic activity of Cu facets and their influence under different pH conditions remain unclear, particularly in the presence of ions commonly found in water such as Cl⁻, Na⁺, Mg²⁺, and Ca²⁺. Using density functional theory (DFT) calculations, we evaluated the NRA pathways on Cu(111), Cu(100), and Cu(110) surfaces across varying pH levels and in the presence of contaminating ions. Our systematic thermodynamic and kinetic analysis revealed that proceeding through *NOH intermediate is the most probable across all pH ranges. We observed that both the catalytic deoxygenation and hydrogenation processes in NRA are substantially affected by pH, and the presence of ions with pH- and ion-dependent rate- determining steps. Furthermore, we found that the presence of ions, especially Cl ions, enhances NO₃ - adsorption on all Cu facets. However, it influences on the rate determining steps differ on each surface, with some steps, such as *NO to *NOH hydrogenation, becoming increasingly unfavorable. Additionally, we investigated NRA pathways on Cu-decorated MXene surfaces. Functionalization led to a significant increase in the NRA catalytic activity of Cu-doped Ti₂C₂O₂ MXenes. These findings offer new strategies for the rational design of MXene-based NRA electrocatalysts with universal significance in environmental and energy-related applications.

Enhancement of CO₂ Reduction Reaction on Two Dimensional Catalysts Supported by a Ferroelectric In₂Se₃ Substrate

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Studies in recent years have shown that ferroelectric materials (i.e., In₂Se₃ or LiNbO₃) can improve the CO₂ reduction reaction (CO₂RR) by breaking limiting scaling relationships and overcoming the Sabatier Principle. Using a switchable out-of-plane polarization (OOP), the adsorption properties and kinetics of the CO₂RR can be controlled on a ferroelectric surface. It was shown that the adsorption energies of CO₂ and CO on a single transition metal (TM) decrease when switching the OOP direction of a supported In₂Se₃ from up to down. Here, we investigated the use of In₂Se₃ as a ferroelectric substrate to support other two dimensional catalyst materials. Graphene doped with single and double transition metal (TM) atom catalysts was investigated as the catalytic material for CO₂RR. The structure and electronic behavior of a single TM-doped graphene/In₂Se₃ (TM = Fe, Cu and Co) heterostructure was studied by performing density functional theory (DFT) calculations; within these systems, C atoms coordinating the TM atoms were also systematically replaced by N. We found that switching the polarization state of In₂Se₃ leads to significant changes in the adsorption strength of the adsorbates and stability of intermediates, while replacing C with N further alters the catalytic properties. Furthermore, a double TM₂-doped graphene/In₂Se₃ heterostructure shows an enhancement in C-C coupling, leading to the possibility of production of C₂ products. Through calculations of the density of states, band structure, charge density, and morphology of the system, we elucidate the reasons underlying the properties of this promising system to catalyze the CO₂RR.

Insights on the mechanistic understanding of the electrochemical reduction of furfural at the electrode-electrolyte interface

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The growth of renewable energy can be advantageous to the chemical manufacturing industry as it provides a door to shift towards sustainable chemical production technologies. The use of renewable electricity as a driving force of a chemical reaction could replace the conventional thermochemical processes and significantly reduce the carbon footprint. Furthermore, renewable electricity can be utilized to produce sustainable chemicals such as the ones obtained from biomass feedstock. Furfural (FF) is one of the biomass-derived chemicals that can be reduced to produce furfuryl alcohol (FA) which is an intermediate to form polymer resins, and 2-methylfuran (MF) which can be used as biofuel to provide energy. Our group has previously reported the electrochemical hydrogenation and hydrogenolysis (ECH) of FF under acidic conditions where MF is more favorable. It was observed that FF ECH followed the non-competitive Langmuir-Hinshelwood kinetic model and the production of FA and MF followed different reaction mechanisms on copper at pH 0-1 and -0.56V RHE. The goal of the current study is to further understand the competing reactions mechanism at the molecular level aided with Attenuated Total Reflectance–Surface Enhanced Infrared Spectroscopy (ATR-SEIRAS). We have utilized in-situ ATR-SEIRAS to investigate the surface reactions occurring at a copper film deposited on a silicone crystal substrate while varying the pH in a range of 2-5. Furthermore, the role of applied potential in determining the reaction mechanism is studied by varying the potential from low to high overpotential (-0.2V RHE to -0.65V RHE). Further understanding on the reaction mechanism at the heterogeneous catalyst interface could foster the development of catalysts that could be tuned to favor the desired FF ECH reaction at particular reaction conditions.

Spectroscopic Elucidation of Phase Evolution in NiO/YSZ and LaFe_{0.9}Ni_{0.1}O₃ under Oxidative and Reductive Gas Environments

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High temperature co-electrolysis of CO₂ and H₂O serves a viable, energy efficient, and scalable route to produce syngas (CO + H₂). The solid oxide electrolysis cell (SOEC) has proven to be a promising technology for CO₂ utilization and a carbon neutral route to curb CO₂ emissions. The design of the cathode catalyst is critical as it must facilitate the activation of CO₂ and H₂O while maintaining redox stability and exhibiting high electronic and oxygen ion conductivity. The state-of-the-art cathode materials used in SOECs are Ni/YSZ (8 mol% Ytria Stabilized Zirconia) ceramic composite and novel perovskite LaFe_{0.9}Ni_{0.1}O₃ (LFNO), with performances dependent on various operating factors including temperature, composition of feed gas stream, presence of contaminants like SO_x/NO_x, etc. With the aim of tracking electrocatalyst's structural evolution and surface chemistry under oxidative and reductive gas compositions at high temperature, the cathode materials Ni/YSZ and LFNO were studied using in situ Raman spectroscopy and High Sensitivity-Low Energy Ion Scattering (HS-LEIS). Typical flue gas composition is chosen on the basis of the concentration of different components like 15% CO₂, 10% H₂O, 5% O₂ with argon. Under H₂, metallic Ni is formed in the Ni/YSZ cathode while the YSZ phase is stable under these conditions at elevated temperature. Exposure to oxidative environments on Ni/YSZ resulted in the formation of a defective NiO_x phase on the stable YSZ. For the LFNO cathode, in situ Raman spectroscopy reveals the reversible nature exsolution of metallic NiFe nanoparticles under H₂ and dissolution in the host lattice under O₂. Surface compositional analyses of the perovskite LaFe_{0.9}Ni_{0.1}O₃ cathode revealed that the surface is dynamic and strongly dependent on the gaseous environmental conditions. The results from this study provide the fundamental insights on the effects of temperature and gas phase composition upon the surfaces and bulk phase of the Ni/YSZ and LFNO cathodes, which serve as a rational guide for the process level design and operation of SOECs.

Physicochemical Changes for ORR Electrocatalysis Enhancement During Nitrogen-doped Graphene with Metal-organic Framework (N-G/MOF) Nanocatalyst Synthesis

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In the effort to develop cost-effective and reliable alternatives to the Platinum Group Metal (PGM)-based electrocatalysts for oxygen reduction reaction (ORR) in electrochemical energy systems, graphene-based materials, particularly nitrogen-doped graphene (N-G), have shown significant promise. Different types of materials are being combined with N-G to induce synergistic effects, leading to highly efficient ORR catalysts with better operational stability. Metal-organic frameworks (MOFs) hold promises for this purpose, given their theoretically advantageous physicochemical forms for ORR catalysis. We have synthesized an N-G/MOF nanocatalyst by combining N-G with a MOF (ZIF-8) through a wet ball milling process applying optimal grinding speed and time. The catalytic performance of N-G/MOF was comparable to a benchmark 10% Pt/C catalyst for ORR; in an alkaline medium N-G/MOF outperformed the benchmark catalyst by generating higher ORR current density. Nonetheless, the intrinsic physicochemical reasons for such an improved catalytic nature of N-G/MOF, in terms of physical and chemical changes that occurred during the synthesis process, are yet unknown. In this study, to track the physical and chemical changes from the precursors (N-G and ZIF-8) to the N-G/MOF catalyst, samples of these materials were comparatively analyzed for pore size, pore volume, BET surface area, elemental composition, and nitrogen functional groups. Higher catalytic performance of N-G/MOF could be related to optimal values of property and surface area. For the point chemical changes, higher nitrogen (N) content and the presence of dispersed zinc (Zn) atoms are likely to enhance the catalytic activity by generating a higher number of active sites. In N-G/MOF the combined relative ratio of pyridinic-N and graphitic-N functional groups was higher (75.04%; among all nitrogen groups) than the precursors. Besides, an increment in the oxidation state of carbon (C) atoms was observed. These chemical changes are likely to enhance the ORR catalysis on the N-G/MOF nanocatalyst.

Kinetic ramifications of metal coordination and solvent environments for alkene oxidation over Fe and Cr carboxylate metal-organic frameworks

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Metal-organic frameworks (MOFs) are active nanoporous catalysts for the oxidative upgrading of unsaturated hydrocarbons, but kinetic mechanisms for many transition-metal MOFs are unknown. Here, we investigate styrene oxidation by hydrogen peroxide (H₂O₂) as a probe reaction on two families of first-row transition metal-based carboxylate MOFs (MIL-101, MIL-100), which both exhibit an MTN zeotype framework with microporous and mesoporous voids. Batch liquid-phase kinetic experiments over Cr- and Fe-based MIL-101 reveal higher styrene oxidation rates over Fe sites compared to Cr sites at 323 K in acetonitrile. Additionally, MIL-101(Fe) is more selective than MIL-101(Cr) for primary product benzaldehyde (Fe: 78±1 %, Cr: 16±1 %) than for the other competing primary product styrene oxide at differential iso-conversion (7 %) points. Selectivity differences observed between MIL-101(Fe) and MIL-101(Cr) are likely rooted in disparate H₂O₂-derived reactive intermediate surface coverages that result in distinct metallocycle transition state structures for each primary product. Solvent effects are investigated for MIL-101(Fe) and MIL-101(Cr) through temperature studies (318-328 K) in acetonitrile and methanol and indicate greater stabilization (1-7 kJ mol⁻¹) of both benzaldehyde and styrene oxide transition states in methanol than in acetonitrile due to H-bonding with surrounding methanol molecules. Beyond solvent environment, coordination environment effects are assessed for a series of isometallic Fe MOFs (NH₂-MIL-101(Fe), MIL-101(Fe), MIL-100(Fe)) for styrene oxidation in acetonitrile at 323 K. Lower styrene oxidation rates in the absence of mass transport effects are observed over NH₂-MIL-101(Fe) and MIL-100(Fe) compared to MIL-101(Fe), which are rooted in combined first and second coordination sphere effects. Overall, this work leverages the tunability of MOF structures to investigate the consequences of metal identity and solvent and coordination environments on observed reactivity and deactivation during alkene oxidation by a mild oxidant.

Understanding reactivity and structural impacts of contrasting earth-abundant metal-organic frameworks in the context of aqueous pollutant oxidation

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Increased water consumption and concomitant rising water pollution motivates continued research to improve the efficacy of wastewater treatment. Metal-organic frameworks (MOFs), consisting of networks of organic linkers coordinated to metal-containing nodes, hold potential for application in adsorptive and oxidative (photo)catalytic removal of aqueous pollutants. MOFs synthesized from earth-abundant metals, such as zirconium(Zr-) and iron(Fe), are particularly attractive because of their low cost and previous demonstration of pollutant abatement. This work focuses on hydrogen peroxide oxidation of model medication and dye methylene blue (MB) to understand connections between structure and function of Zr- and Fe-MOFs in the removal of pollutants pertinent to industrial effluent. Under excess oxidant conditions, MIL-101(Fe) demonstrates a lumped first order rate constant (normalized by total Fe) over three times that of contrasting MOF-235 constructed from the same secondary building units in different crystallographic arrangement (MTN zeotype vs. acs topology, respectively) likely resulting from disparate ligands coordinated to their metal nodes. However, loss in crystallinity and Fe leaching are evident, even though the catalysts continue to degrade dye after recovery and reuse. Moreover, the dominant role of solvent interactions in causing these changes is implicated by leaching occurring through catalyst exposure to water alone, with framework breakdown likely driven by hydrolytic cleavage of network bonding. In contrast, Zr-based UiO-67 retains its long-range order after exposure to water. Addition of Fe-oxide nanoparticles and dispersed Fe moieties to UiO-67 via incipient wetness impregnation or pore size modulation through synthesis of UiO-68 (longer linker) decreases MOF band gap energy, allowing for enhanced photocatalytic degradation of MB at lower energy wavelengths. Continued development of hybrid structures using earth-abundant metal source MOFs demonstrates a promising route forward in refining their structure and use in wastewater treatment applications.

Transient kinetics infrared reflection absorption spectroscopy studies of NO on Pd(111)

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Transient kinetics studies of NO adsorption, reaction, and desorption on Pd(111) are carried out using a novel approach involving square waves of NO exposure while acquiring infrared reflection absorption spectra with high temporal resolution. The well-defined pressure waves are possible using a fast-dosing valve (100's microsecond time resolution) connected to a capillary tube directing the molecules at the sample surface. Tracking the time-resolved spectra allows for mechanistic studies of the elementary steps of the different pathways this reaction can take. In this work, we will discuss the experimental setup and the results from the study in comparison with prior literature. We have performed experiments at different temperatures and observed two peaks and the dynamics of these two peaks are quite fascinating. The evolution of these peaks will be discussed in details.

Transition Metal Pnictides: Bioinspired Electrocatalysts for Converting CO₂ to Multi-carbon Products from Scratch

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With global energy demand and CO₂ emissions ever-growing, there is an urgent need to develop cleaner sources of chemicals and fuels to mitigate climate change. High overpotentials, poor product selectivity, and unknown reaction mechanisms have restricted the development of commercial electrocatalytic processes for reducing carbon dioxide (CO₂RR) to multi-carbon products. This talk will develop the intellectual framework and catalyst examples for making multi-carbon molecules from scratch, using only CO₂ and water as material inputs. Transition Metal Pnictides (TMPs) are solid-state compounds containing elements from the transition metals (3d, 4d) and group-15 Pnictides (P, As). They are inspired by the exergonic class of enzymes that have evolved by natural selection, specifically for efficient CO₂ reduction and C-C coupling at ambient temperature. These catalysts use electricity to populate electronic states with electrons at energies just above the Fermi level. These states can either react with protons or water to form surface hydrides (*H), or increase the binding affinity of CO₂ and intermediates by charge transfer, so-called potentiometric activation. No thermal activation is needed or desired, as this lowers selectivity. TMPs differ from strongly conducting metals like copper, which form no surface hydrides, and perform reduction of CO₂ by delivering electrons instead of hydrides. The heterolytic bond dissociation enthalpy (hydricity) of these *H and their ionic vs covalent bond character governs the reducing potential of these hydrides, which determines the extent of reduction. Productselectivity – the discrimination amongst C1, C2, C3, C4, and polycarbonate polymer – as well as the reaction rate are determined by the TMP's ability to facilitate C-C couplings (aldol vs. C₂dimerization, etc.), isomerization (keto-enol, etc.) and substitutions/additions (dehydration, anation). We shall illustrate the newest class of TMPs (3d, 4d and group-15) electrocatalysts that produce systematic changes in product selectivity. Funded by the DOE-STTR program.

Design of ordered mesoporous oxides for dielectric barrier discharge-assisted catalysis of ammonia synthesis

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Industrial Haber-Bosch ammonia synthesis entails high temperatures and pressures, resulting in significant carbon emissions when fossil-powered that can potentially be reduced by direct electrification, for example through non-thermal plasma-assisted catalysis. Studies using packed bed dielectric barrier discharge (DBD) reactors have shown that metal nanoparticles supported on porous oxides can have nitrogen conversions similar to those on metal-free porous oxides alone, indicating there are significant support contributions that need to be understood to overcome the current low energy yields of DBD-assisted catalysis. Synthetically controlled pore sizes and surface areas of ordered mesoporous materials (OMMs), like the silica-based SBA-15, maintain material composition while systematically probing porosity effects on nitrogen conversion and DBD properties. However, γ -alumina supports are more desirable than silica supports due to their higher reported nitrogen conversions and ammonia adsorption on acid sites that potentially shields ammonia from decomposition by the plasma. Thus, we synthesized γ -alumina-coated SBA-15 (5-15 wt. % Al) via a reported wetness impregnation procedure which preserves the ordered porosity of SBA-15, based on FTIR and nitrogen physisorption data. The OMMs were pelletized prior to testing in our DBD reactor (for a more homogenous discharge), where they exhibited higher nitrogen conversions than pelletized powders of non-ordered oxides, extending insights in literature for ordered silica to γ -alumina. Higher nitrogen conversions were also measured on OMM pellets relative to commercial pellets, despite lower measured electron densities on the pellets (likely due to inhibited plasma generation within smaller interparticle voids). Ex situ temperature programmed desorption measurements on the catalysts showed the highest ammonia uptake for the composite supports, highlighting their potential ability to shield ammonia from undesired decomposition in the plasma. Together, these results inform the rational design of OMM porosity and surface functionality to optimize DBD properties, catalytic activity, ammonia uptake, and energy yield of DBD-assisted catalysis of ammonia synthesis.

Active Site Identification, CO Oxidation, and Non-Thermal Plasma Reduction of Catalytic MOF Nanofilms

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The need for efficiency and productivity in industry has demanded the development and application of novel solid catalysts whose active sites can be fundamentally studied. Metal-organic frameworks (MOFs) offer an intrinsically porous and chemically tunable platform for gas adsorption, separation, and catalysis. We investigate thin film derivatives of the well-studied Zr–O based MOF powders to understand their adsorption properties and reactivity with their adaption to thin films, involving diverse functionality with the incorporation of different linker groups and the inclusion of embedded metal nanoparticles: UiO-66, UiO-66-NH₂, and Pt@UiO-66-NH₂. Using transmittance IR spectroscopy, we determine the active sites in each film and perform metal-based catalysis with CO oxidation of a Pt@UiO-66-NH₂ film. Furthermore, we expand the use of transmittance IR to study the effect of non-thermal plasma in-situ on the Cu-based MOF HKUST-1, with plans to study catalytic reactions with nonthermal plasma. The effect of H₂ and CO plasma on the Cu oxidation state and the framework ligands were investigated. Our study shows how surface science characterization techniques can be used to investigate the reactivity and the chemical and electronic structure of MOFs.

Studies on the Synthesis, Reactivity, and Stability of Au Nanoparticles in Ti-MFI Zeolites for Propylene Epoxidation within H₂/O₂ Mixtures

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Encapsulated Au nanoparticles in Ti-MFI zeolites (denoted Au@Ti-MFI) were prepared via a ‘one-pot’ hydrothermal synthesis method by using 3-mercaptopropyl-trimethoxysilane to chemically protect Au³⁺ precursors from precipitation and reduction while also promoting nucleation of silicate oligomers around the ligated metal species during zeolite crystallization. Syntheses were carried out between 100-140 °C for 46-63 hours while rotating at 50 RPM. The as-made zeolites (Si/Ti molar ratios ~100, ~0.2-0.5 wt.% Au) endured a sequence of thermal treatments to remove the organic precursors and form encapsulated Au nanoparticles with volume-area-weighted mean particle diameters ranging from 6-10 nm as estimated by HR-STEM analysis. Catalyst deactivation and steady-state kinetics measurements were performed during propylene epoxidation in the presence of H₂ and O₂ at 1 atm over a temperature range of 120-200 °C in a catalytic testing unit equipped with a U-shaped fixed bed reactor and a gas recirculation system to maintain propylene conversion within the differential limit of < 10% and account for inhibition by reaction products. Kinetic results showed that steady-state PO rates at 200 °C (H₂:O₂:C₃H₆:N₂ = 10:10:10:70 (vol%), 36 cm³ min⁻¹) ranged from ~15-35 gPO h⁻¹ (kgcat) ⁻¹ for Au@Ti-MFI, accounting for inhibition by PO, compared to ~2.5 gPO h⁻¹ (kgcat) ⁻¹ for Au/Ti-MFI catalysts prepared by either deposition-precipitation (DP) or strong electrostatic adsorption (SEA). PO selectivities for Au@Ti-MFI, Au/Ti-MFI (DP), and Au/Ti-MFI (SEA) ranged from 98.5-99.7%, consistent with reported selectivities > 95% for Au/Ti-MFI (DP). The increase in PO rates over Au@Ti-MFI compared to Au/Ti-MFI (DP) and Au/Ti-MFI (SEA) is attributed to the formation of stable Au nanoparticles anchored in close proximity to Ti sites within the support. Moreover, the presence of alkali cations during synthesis leads to measurable differences in Au particle size and reactivity. Au@Ti-MFI with 0.36 wt.% K contained ~10 nm Au particles sizes and demonstrated higher steady-state PO rates (~25 gPO h⁻¹ (kgcat) ⁻¹), compared to Au@Ti-MFI with 0.01 wt.% K and ~6 nm Au particles (~12 gPO h⁻¹ (kgcat) ⁻¹).

Investigating key parameters for polynitrogen synthesis

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Polynitrogen (PN) species and compounds are chain-like arrangements of nitrogen atoms that are building blocks for three-dimensional crystalline structures. Polynitrogen (PN) as highly energetic materials have attracted many theoretical calculations and predictions. Some researchers have experimentally observed N₃, N₄, N₅ or their ions in the gas phase at extreme conditions. Recently, a single, zigzag N₈ chain of nitrogen atoms was theoretically shown to be stable inside carbon nanotubes and between sheets of graphene. Experimental synthesis of PN compounds however remains difficult. An N₈ with C_{2h} symmetry was successfully synthesized by our group using a cyclic voltammetry (CV) method. Our initial work showed PN is a metal free, “green”, and cost-effective oxygen reduction reaction (ORR) cathode catalyst for PEM fuel cells and the ORR performance depends on the PN amounts on the carbon nanotube substrate. Hence, this study seeks to maximize the amount of PN generated by investigating several key parameters. Different buffers, precursors, and working electrodes were scrutinized to determine their effect on the PN synthesis and thus the ORR performance. It is found that the type of buffer solution, type of electrode and electrode size have significant effect on the PN yield.

Electrocatalytic CO₂ Reduction on Single Crystal NiP₂ Facets: Surface Intermediates and Mechanism Revealed

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The electrochemical CO₂ reduction reaction (CO₂RR) on transition metal phosphides produces multi-carbon products under mild conditions that are carbon-negative replacements for petrochemical feedstocks. Grand Canonical (GC)-DFT studies on nickel phosphides predict that formation of phosphino-hydride bonds (P-H) are key for CO₂RR catalysis, though experimental evidence is lacking. Here, we employ atomically flat single-crystal facets of NiP₂ (11-1) facet of standardized C2/c space group) to investigate the dependence of CO₂RR performance, the reaction mechanism, and the vibrational modes of adsorbates using in-situ Raman spectroscopy. Under an electrical bias such as used for CO₂RR, two peaks appear at 1060 cm⁻¹ and 687 cm⁻¹ that are identified by model compounds and DFT-derived normal mode analysis as surface hydride (PH₂) or hydroxyl P(OH)₂ vibrational modes. H/D isotopic studies are in progress to distinguish these possibilities. The results from CO₂RR product analysis show that only a single C₃ product, methylglyoxal, forms on the (11-1) facet, in contrast to three products on multi-faceted polycrystalline particles [C₁-formic acid (FA) << C₃-methylglyoxal (MG) ~ 2,3-furandiol (FD)]. We previously determined the mechanism on polycrystalline facets and found there is a kinetic or energy barrier to the MG→FD aldol condensation step on the (11-1) basal planes that prevents FD formation, thereby explaining the singular product on (11-1). Further mechanistic work on NiP₂ and other TMP electrocatalysts has the potential to produce carbon-negative chemicals by design from scratch. Supported by a DOE-SBIR contract.

Catalytic Selective Hydrogenation of Aromatic Hydrocarbons to Cycloolefins

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Hydrogenation of aromatic hydrocarbons to cycloolefins is required in the production of numerous and diverse commodity and specialty chemicals. In the absence of efficient catalysts, the chemical, pharmaceutical and food industries are currently using multistep complex processes that involve hazardous and environmentally-unfriendly intermediates and byproducts. In this work, efficient bimetallic palladium catalysts for selective hydrogenation of aromatic hydrocarbons into cycloolefins were developed. Adsorption sites and hydrocarbon surface species were determined. Selectivity improvements were attributed to changes in relative adsorption energies between the initial aromatic hydrocarbon and the cycloolefin product. A series of palladium catalysts on multiple supports were prepared using the incipient wetness impregnation method. Effects of the support and catalyst pretreatments were examined. In addition to pure palladium, bimetallic palladium catalysts were also evaluated. Selective hydrogenation of an aromatic hydrocarbon 1,1,2,3,3-pentamethyl indane (PMI) to the corresponding cycloolefin 1,1,2,3,3-pentamethyl-tetrahydro indane (THPMI) in liquid phase was used as the probe reaction. The catalysts were characterized with transmission electron microscopy (TEM), scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM-EDS), X-ray diffraction (XRD) and temperature programmed desorption (TPD) measurements. The experimental study was combined with density functional theory (DFT) calculations for elucidating the adsorption and surface reactivity of the aromatic and cycloolefin hydrocarbons.

Microkinetic Modeling-driven Density Functional Theory Exploration of Ethylene Epoxidation on Partially Oxidized Silver Catalyst Surfaces

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Overcoming the selectivity challenge in the selective oxidation of ethylene has been an ongoing decades-long journey which has been partially addressed through the utilization of a slew of Ag catalyst promoters from across the periodic table. Despite their proven efficacy, there is a lack of systematic understanding in the promotion of the catalyst, and detailed effects of combinations of promoters are not well understood. Additionally, there has been a reinvigorated push towards a more careful study of the oxidic reconstruction of the Ag surface during the reaction. These concerns guide the three focal points of the current study: 1) Extension of the ethylene oxidation (EO) reaction mechanism to account for partially oxidized surfaces, 2) Analysis of promoter effects on specific elementary steps in the extended mechanism, and 3) ab-initio simulations supplement for atomic-level details in both unpromoted & promoted cases.

One pathway to oxidize C_2H_4 involves the surface lattice O atom of a partially oxidized Ag surface, through which an oxygen vacancy ($/O^*$) is generated. A subsequent adsorption of O_2 into the $/O^*$ site, forms a new oxygen species (O_2/O^*). An extended MKM is constructed to validate the possible kinetic relevance of these new intermediate species to the EO reaction system, featuring the currently-accepted common-intermediate mechanism, additional reaction pathways involving both the $/O^*$ and O_2/O^* species, and ethylene oxidation on Ag_6 patches. Here, the ‘ Ag_6 ’ notation is used to represent the metallic portion of the $p(4 \times 4)$ -O-Ag(111) surface, which features 6 exposed Ag atoms. The current work explores the competition between these three pathways, along with the effects of common catalyst promoters on them.

Elucidating the essential role of hydrogen bonding and direct H-transfer in transfer hydrogenation on transition metal catalysts

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Hydrogenation and hydrogenolysis, two important catalytic chemistries employed in the chemical industry, are typically carried out at high pressure using gaseous molecular hydrogen as the hydrogen source. Catalytic transfer hydrogenation (CTH), is an alternative process that employs organic hydrogen donors such as alcohols and formic acid (FA) as the hydrogen source, offering a safer and milder option for small-scale and distributed processing, such as for biomass conversion. The underlying mechanism of such reactions is not fully understood. In particular, CTH may occur through an indirect “metal hydride route” where the donor dehydrogenates on a metal surface and the surface hydrogen atoms get picked by the acceptor molecule; alternatively, donors may directly transfer hydrogen to the acceptor, especially on Lewis acid catalysts.

In this presentation, we use FA as a representative hydrogen donor and formaldehyde as a representative hydrogen acceptor to elucidate how hydrogen bonding affects the reaction mechanism for CTH of carbonyl bonds on Cu(111). Using dispersion-corrected periodic density functional theory (DFT, PBE-dDSC) calculations and coverage-cognizant mean-field microkinetic modeling, we develop a mechanistic model of this CTH system. We show that direct hydrogen atom transfer between a donor and acceptor is kinetically feasible on transition metal catalysts especially if the donor and the acceptor can interact via hydrogen bonding. Such direct transfer significantly enhances the rate of catalytic hydrogenation by 3 times while using a hydrogen donor relative to using molecular hydrogen as the hydrogen source. This work, thus, indicates the potential tuning of activity and selectivity of hydrogenation through judicious choice of hydrogen donors.

Thermodynamic and Kinetic Investigation of S Impurities in Solid Oxide Electrolysis Cell Feed Flow

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Solid Oxide Electrolysis Cells (SOECs) have become a system of interest due their efficiency of splitting H₂O and reducing CO₂ into useful products. Catalytic activity on Ni/YSZ cathodes can be hampered by the presence of S constituents in feed flows. Here, we seek to analyze the surface reactions which produce desired, useful, products and undesired products on Ni(111), Yttria-stabilized Zirconia (YSZ), and Ni/YSZ facets. The reduction of H₂O, the reduction of CO₂, and the dissociation of S containing species under reaction conditions (~1070K) are investigated in order to quantify the energetics of these reactions and their intermediates. Using these findings a microkinetic model can be created to understand the effects of S and S containing species on cathode reactions using a combination of Density Functional Theory (DFT) and Transition State Theory.

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