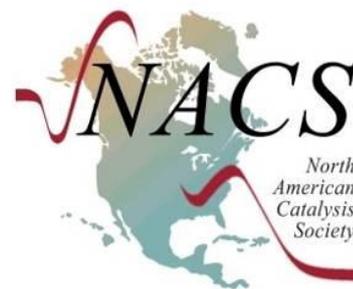
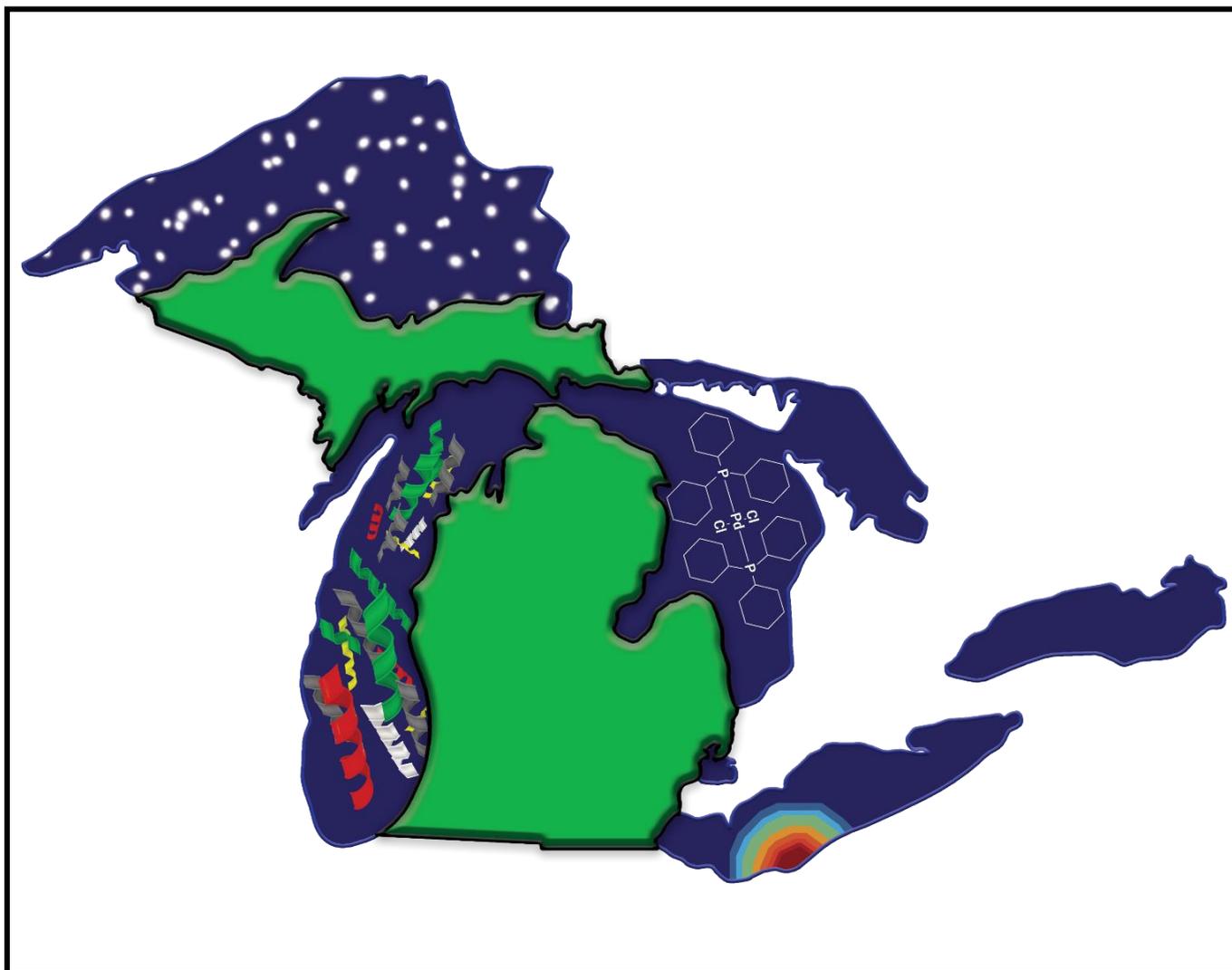




42nd Annual MC-NACS Symposium



Wednesday, September 29, 2021



Virtual Conference via Zoom. Link will be sent to registered participants.

**THE MICHIGAN CHAPTER OF THE NACS
42nd ANNUAL SYMPOSIUM**

Wednesday, September 29, 2021

Morning Session:	Ming Yang, President
08:30 – 08:35	Welcome and Opening Remarks by Ming Yang, Clemson University
08:35 – 08:40	Introduction of Invited Speaker by Ming Yang
08:40 – 09:30	Invited Lecture Single Atom Catalysis: From an Academic Curiosity to Industrial Applications, <u>Abhaya K. Datye</u> , <i>University of New Mexico</i>
09:30 – 9:50	Predicting the Stability Metrics of Generic Nanocatalysts and their Uncertainties On-The-Fly, <u>Tej Chokski</u> , <i>Nanyang Technological University, Singapore</i>
09:50 – 10:10	Accumulation and Nature of a Thermodynamically-stable PtO_xH_y Interface on Pt(111) During CA Between 0.5 and 1.1 V_{RHE}, <u>Arthur J. Shih</u> , <i>Leiden University, Leiden, The Netherlands</i>
10:10 – 10:20	Break / buffer
10:20 – 10:40	Investigating Surface and Gas-phase Chemistries during the Boron Nitride-catalyzed Oxidative Dehydrogenation of Propane, <u>Juan M. Venegas</u> , <i>University of Wisconsin</i>
10:40 – 11:00	Machine-Learning Interpretable Chemisorption Models for Alloys, <u>Jacques Esterhuizen</u> , <i>University of Michigan</i>
11:00 – 11:20	Oxygen Electrocatalysis by Non-Stoichiometric Mixed Metal Oxides: Avenues for Engineering Active and Stable Cationic Centers, <u>Samji Samira</u> , <i>Wayne State University</i>
11:20 – 11:40	Influence of Anions on Charge Transfer in Redox Couples for Flow Batteries, <u>Harsh Agarwal</u> , <i>University of Michigan</i>
11:40 – 12:00	CeO_x-Cu-Based Catalysts for CO₂ Hydrogenation, <u>Ibeh S. Omodolor</u> , <i>The University of Toledo</i>
12:00 – 1:00	Lunch break
Afternoon Session:	Krishna Janmanchi, Vice-President
1:00 – 1:10	Parravano Award Presentation by Johannes Schwank
1:10 – 2:00	Parravano Award Lecture Embracing the Complexity of Heterogeneous Catalytic Structures: Catalysis by Nonstoichiometric Mixed Metal Oxides and 3-Dimensionally Engineered Metal Catalysts, <u>Eranda Nikolla</u> , <i>Wayne State University</i>
2:00 – 2:20	Electrocatalytic Nitrate Reduction to Ammonia on Metals and Alloys, <u>Bryan R. Goldsmith</u> , <i>University of Michigan</i>

- 2:20 – 2:40 **A First Principles Analysis to Understand the Potential Dependent Reaction Mechanism of Ethanol Electro-oxidation on Pt(100) surface,** Siddharth Deshpande, *Purdue University*
- 2:40 – 3:00 **Leveraging Encapsulated Morphologies to Improve Catalytic Activity and Durability,** Alexander Hill, *University of Michigan*
- 3:00 – 3:10 Break / buffer
- 3:10 – 3:20 **CO₂ Capture and Conversion with Dual-Function Materials,** Ana C. Alba-Rubio, *The University of Toledo*
- 3:20 – 3:30 **Rhodium Single-atom Catalysts on Titania for Reverse Water Gas Shift Reaction Explored by First Principles Mechanistic Analysis and Compared to Nanoclusters,** Francis J. Doherty, *University of Michigan*
- 3:30 – 3:40 **Examining Pd Small-Pore Zeolites for Low-Temperature Catalytic Oxidation of Methane,** Jingzhi Liu, *Syracuse University*
- 3:40 – 3:50 **Synergizing Atomically Dispersed Fe and Mo-Nitrogen Coordinated Active Sites for Efficient Electrochemical Nitrate Reduction to Ammonia,** Eamonn C. Murphy, *University of California, Irvine*
- 3:50 – 4:00 **The Reaction Pathway of Propane Conversion to Higher Molecular Weight Hydrocarbons Using a PtZn/SiO₂+H-ZSM-5 Bifunctional Catalyst,** Che-Wei Chang, *Purdue University*
- 4:00 – 4:10 **Electrocatalytic Nitrate Reduction on Rhodium Sulfide Compared to Pt and Rh in the Presence of Chloride,** Danielle Richards, *University of Michigan*
- 4:10 – 4:20 **Computational Investigation and Quantification of Active Cu Sites in Cu-SSZ-13 Zeolite for Selective Activation of Methane,** Yujia Wang, *University of Notre Dame*
- 4:20 – 4:30 **Understanding Aqueous-phase Adsorption and Hydrogenation of Phenol on Pt and Rh from First Principles,** Isaiah Barth, *University of Michigan*
- 4:30 – 4:40 **Examining Acid-Base Cooperativity in Zeotype Catalysts to Direct Cross-Aldol Condensation Reactions between Aldehydes,** Wenlin He, *Syracuse University*
- 4:40 – 4:50 **Consequences of and Models for Incorporating Coverage-dependence into Microkinetic Models,** Anshuman Goswami, *University of Notre Dame*
- 4:50 – 5:00 **Synthesis and Intrinsic Electrocatalytic Activity Evaluation of Ni_{2-x}Rh_xP Nanoparticles for Water Splitting Reactions in Basic Media,** Tharanga N. Batugedara, *Wayne State University*
- 5:00 – 5:10 Final Remarks and Introducing New Officers by Ming Yang, President

Eranda Nikolla, Ph.D.



The 2021 Michigan Catalysis Society Parravano Memorial Award for Excellence in Catalysis Research and Development

Eranda Nikolla is a Professor in the Department of Chemical Engineering and Materials Science at Wayne State University. She is also an Associate Editor for the Journal of Catalysis. Her research group at Wayne State University focuses on the development of heterogeneous catalysts/electrocatalysts for chemical and energy conversion/storage processes using a combination of experimental and theoretical techniques. She received her Ph.D. in Chemical Engineering from University of Michigan in 2009 working with Prof. Suljo Linic and Prof. Johannes Schwank in the area of solid-state electrocatalysis. She conducted a two-year postdoctoral work at California Institute of Technology with Prof. Mark E. Davis prior to joining Wayne State University. At Caltech, she developed expertise in the synthesis and characterization of meso/microporous materials and functionalized surfaces. Her group's impact to catalytic science has been recognized through the National Science Foundation CAREER Award, the Department of Energy Early Career Research Award, Camille Dreyfus Teacher-Scholar Award, the Young Scientist Award from the International Congress on Catalysis, and the 2019 ACS Women Chemists Committee (WCC) Rising Star Award.

Abhaya Datye, Ph.D.



2021 MC-NACS Symposium Invited Lecturer

Abhaya Datye has been on the faculty at the University of New Mexico since 1984 after receiving his Ph.D. in chemical engineering from the University of Michigan, working with Johannes Schwank. He has authored 247 publications, 7 patents and has presented 166 invited lectures around the world. His published work has received ~16,885 citations with an *h-index* of 67 (Google Scholar). He is a fellow of the AIChE, the Microscopy Society of America and the Royal Society of Chemistry. He has been actively involved in the North American Catalysis Society, serving as co-chair for the Denver NAM 2017, program co-chair for the Snowbird NAM 1995 and Vice Chair for the ICC 2020. He was the Chair of the Gordon Research Conference on Catalysis in 2010.

His research group has pioneered the development of electron microscopy tools for the study of catalysts. His current work involves fundamental studies of catalyst sintering, especially the stabilization of isolated single atoms on supports for high temperature catalytic applications such as exhaust catalysis and alkane dehydrogenation. His research has been recognized through numerous awards, including the Robert L. Burwell Lectureship of the North American Catalysis Society (2019), Walter J Weber Distinguished Lectureship from the University of Michigan Chemical Engineering (2019), Eastman Lectureship from the University of South Carolina (2019) and the John Matthews Lectureship from the Microscopy Society of South Africa (2012) and the 2008 Award for Excellence from the NSF IUCRC program. In 2016, the ACS publication Chemical & Engineering News included his research on single atom catalysis as one of the top 10 stories for the year.

THE MICHIGAN CHAPTER OF THE NACS OFFICERS, 2019 - 2021

President:	Ming Yang Clemson University
Treasurer:	Krishna Janmanchi Dow Inc.
Secretary:	Bryan R. Goldsmith University of Michigan, Ann Arbor
MCS Representative to the North American Catalysis Society:	Eric Stangland Dow Inc.
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	Stephanie Brock Wayne State University
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ELECTED NACS OFFICERS for 2021 - 2022

President:	Krishna Janmanchi Dow Inc.
Vice-President:	Bryan R. Goldsmith University of Michigan, Ann Arbor
Treasurer:	Nirala Singh University of Michigan, Ann Arbor
Secretary:	Kevin Gu General Motors Company
MCS Representative to the North American Catalysis Society:	Eranda Nikolla Wayne State University
Board of Directors:	Ming Yang Clemson University
	Stephanie Brock Wayne State University
	Galen Fisher University of Michigan

PAST OFFICERS OF THE MICHIGAN CATALYSIS SOCIETY

<u>YEAR</u>	<u>PRESIDENT</u>	<u>VICE-PRESIDENT</u>	<u>SECRETARY/TREASURER</u>
1977-78	Mordecai Shelef	Alan Brenner	Kathleen Taylor
1978-79	Alan Brenner	Kathleen Taylor	Klaus Otto
1979-80	Kathy Taylor	Klaus Otto	George Tsigdinos
1980-81	Klaus Otto	George Tsigdinos	Craig Murchison
1981-82	George Tsigdinos	Craig Murchison	Richard Herz
1982-83	Craig Murchison	Richard Herz	Johannes Schwank
1983-84	Richard Herz	Johannes Schwank	William Dianis
1984-85	Johannes Schwank	William Dianis	Robert McCabe
1985-86	William Dianis	Robert McCabe	Thomas Pinnavaia
1986-87	Robert McCabe	Thomas Pinnavaia	Robert Stowe
1987-88	Tom Pinnavaia	Robert Stowe	M. David Curtis
1988-89	Robert Stowe	M. David Curtis	Gregory Schmidt
1989-90	M. David Curtis	Gregory Schmidt	Simon Ng
1990-91	Gregory Schmidt	Simon Ng	Dennis Hucul
1991-92	Simon Ng	Dennis Hucul	Galen Fisher
1992-93	Dennis Hucul	Galen Fisher	Levi Thompson
1993-94	Galen Fisher	Levi Thompson	Simon Bare
1994-95	Levi Thompson	Simon Bare	George Graham
1995-96	Simon Bare	George Graham	Alan Brenner
1996-97	George Graham	Alan Brenner	Larry Ito
1997-98	Alan Brenner	Larry Ito	Hung-Wen Jen
1998-99	Larry Ito	Hung-Wen Jen	John Gohndrone
1999-00	Hung-Wen Jen	John Gohndrone	Diana Phillips
2000-01	John Gohndrone	Diana Phillips	David Barton
2001-02	Diana Phillips	David Barton	John Li
2002-03	David Barton	John Li	Wei Li
2003-04	John Li	Wei Li	Eric Stangland
2004-05	Wei Li	Eric Stangland	John Hoard

<u>YEAR</u>	<u>PRESIDENT</u>	<u>VICE-PRESIDENT</u>	<u>SECRETARY/TREASURER</u>
2005-06	Eric Stangland	John Hoard	Jong H Lee
2006-07	John Hoard	Jong H Lee	Suljo Linic
2007-08	Jong H Lee	Suljo Linic	Paul Fanson
2008-09	Suljo Linic	Paul Fanson	Steven Schmieg
2009-10	Paul Fanson	Steven Schmieg	Beata Kilos
2010-11	Steven Schmieg	Beata Kilos	Joe Theis
2011-12	Beata Kilos	Joseph Theis	Chang Kim
2012-13	Joseph Theis	Chang Kim	Eranda Nikolla
2013-14	Chang Kim	Eranda Nikolla	Ted Calverley
2014-15	Eranda Nikolla	Ted Calverley	Hongfei Jia
2015-16	Ted Calverley	Hongfei Jia	Vladimir V. Pushkarev
2016-17	Hongfei Jia	Vladimir V. Pushkarev	Bean Getsoian
2017-18	Vladimir V. Pushkarev	Bean Getsoian	Ming Yang
2018-19	Bean Getsoian	Ming Yang	Ana C. Alba-Rubio
2019-2020	Ming Yang	Krishna Janmanchi	Bryan R. Goldsmith

PAST MCS REPRESENTATIVES TO THE NORTH AMERICAN CATALYSIS SOCIETY

<u>YEAR</u>	<u>NACS REPRESENTATIVE</u>
1995-2001	Craig Murchison
2001-2014	Galen Fisher
2014-present	Eric Stangland

Giuseppe Parravano Memorial Awards

The Michigan Catalysis Society has two awards to recognize individuals who have made outstanding contributions to catalysis research and development. Both awards are sponsored by the Memorial Trust Fund for Professor Giuseppe Parravano, which has been established at the Department of Chemical Engineering, University of Michigan. The Michigan Catalysis Society administers both awards which are presented in alternating years. Both awards consist of a medal and a prize of \$1000. The two awards differ only in the eligibility rules. The recipient of the award is selected by a committee that is appointed by the vice president of the Michigan Catalysis Society.

- 1. The Michigan Catalysis Society Giuseppe Parravano Memorial Award for Excellence in Catalysis Research**

The award is given biennially to an individual from North America to formally recognize outstanding contributions to catalytic science and technology.

- 2. The Michigan Catalysis Society Parravano Memorial Award for Excellence in Catalysis Research and Development**

The award is given biennially to formally recognize outstanding contributions to catalytic science and technology by researchers in the greater Michigan area. To be eligible, a person must be a resident of Michigan or a neighboring area such as western Ontario/northern Ohio and be nominated by a member of the Michigan Catalysis Society.

MCS Giuseppe Parravano Memorial Award Winners

	The Michigan Catalysis Society Parravano Memorial Award for Excellence in Catalysis Research and Development		The Michigan Catalysis Society Giuseppe Parravano Memorial Award for Excellence in Catalysis Research
*1983	Mordecai Shelef Scientific Research Labs Ford Motor Company		
*1984	Alan Brenner Dept. of Chemistry Wayne State University	1985	W. Nicholas Delgass Dept. of Chemical Engineering Purdue University
1986	Klaus Otto Scientific Research Labs Ford Motor Company	1987	Lanny D. Schmidt Dept. of Chem. Eng. & Mater. Sci. University of Minnesota
1988	Craig Murchison Corporate R & D The Dow Chemical Company	1989	W. Henry Weinberg Div. of Chem. & Chem. Eng. California Institute of Technology
1990	John L. Gland Dept. of Chemistry The University of Michigan	1991	Israel E. Wachs Zettlemoyer Ctr. for Surface Studies Lehigh University
1992	Peter R. Norton Dept. of Chemistry University of Western Ontario	1993	J. Michael White Dept. of Chemistry The University of Texas
1994	Johannes W. Schwank Dept. of Chemical Engineering The University of Michigan	1995	Wolfgang M. H. Sachtler Dept. of Chemistry Northwestern University
1996	Robert W. McCabe Scientific Research Labs Ford Motor Company	1997	Raymond J. Gorte Dept. of Chemical Engineering The University of Pennsylvania
1998	Galen B. Fisher Research Laboratories General Motors Corporation	1999	James A. Dumesic Dept. of Chemical Engineering University of Wisconsin
2000	Robert A. Stowe Bobcat Technologies, Ltd	2001	D. Wayne Goodman Dept. of Chemistry Texas A&M University
2002	Thomas J. Pinnavaia Dept. of Chemical Engineering Michigan State University	2003	Bruno Notari Dept. of Chemical Engineering Northeastern University

2004	Dennis A. Hucul The Dow Chemical Company	2005	Bruce C. Gates Dept. of Chemical Engineering & Materials Science University of California-Davis
2006	Levi T. Thompson, Jr. Dept. Of Chemical Engineering University of Michigan	2007	Alexis T. Bell Dept. of Chemical Engineering University of California-Berkeley
2008	George W. Graham Ford Motor Company	2009	Mark A. Barteau Dept. of Chemical Engineering University of Delaware
2010	Guo-Shuh John Lee The Dow Chemical Company	2011	Jens Nørskov Dept. of Chemical Engineering Stanford University
2012	Hung-Wen Jen Ford Motor Company	2013	Maria Flytzani-Stephanopoulos Dept. of Chemical & Biological Engineering Tufts University
2014	Phillip Savage Dept of Chemical Engineering University of Michigan	2015	Jingguang Chen Dept. of Chemical Engineering Columbia Univeristy
2016	Suljo Linic Dept of Chemical Engineering University of Michigan	2017	Manos Mavrikakis Dept. of Chemical & Biological Engineering University of Wisconsin-Madison
2018	William F. Schneider Dept of Chemical and Biomolecular Engineering University of Notre Dame	2019	Fabio H. Ribeiro Davidson School of Chemical Engineering Purdue University
2020	N/A COVID-19	2021	Eranda Nikolla Department of Chemical Engineering and Materials Science Wayne State University

* Originally presented as the Michigan Catalysis Society Award for Excellence in Catalysis Research and Development. This award has been continued under the sponsorship of the Parravano Memorial Trust Fund at University of Michigan.

Past Outstanding Student Presentation Award Recipients

- 1990 Carolyn L. Parks, Wayne State University
- 1991 Sangho Lee, Wayne State University
- 1992 Jean-Remi Butruille, Michigan State University
- 1993 Ben Brosilow, The University of Michigan
- 1994 Kendrick Curry, The University of Michigan
- 1995 Gregory M. Dole, The University of Michigan
- 1996 Anis Barodawalla, Michigan State University
- 1997 Carla E. Hori, Wayne State University
- 1998 Yisun Cheng, The University of Michigan
Chuck Roe, Michigan Technological Institute
- 1999 John Cavataio, The University of Michigan
- 2000 Jeremy Patt, The University of Michigan
- 2001 Christopher Bennet, The University of Michigan
- 2002 Chang H. Kim, The University of Michigan
- 2003 Easwar Ranganathan, The University of Michigan
- 2004 Randolph C. McGee, The University of Michigan
- 2005 Worajit Setthapun, The University of Michigan
- 2006 Eranda Nikolla, The University of Michigan (presentation)
Timothy King, The University of Michigan (poster)
- 2007 Hui Wang, Michigan State University (presentation)
Hongliang Xin, The University of Michigan (poster)
- 2008 Phillip Christopher, The University of Michigan (presentation)
Andrew Smeltz, Purdue University (poster)
- 2009 David Ingram, The University of Michigan (presentation)
Peter Aurora, The University of Michigan (poster)
- 2010 Michael Katz, The University of Michigan (presentation)
Paul Dietrich, Purdue University (poster)
- 2012 Lei Wang, Tsinghua University (presentation)
Shane A. Bates, Purdue University (poster)
- 2013 Adam Holewinski, University of Michigan (presentation)
Timothy Van Cleve, University of Michigan (poster)
- 2014 Atish A. Parekh, Purdue University (presentation)
Harshavardhan J. Chaudhari, Purdue University (poster)
- 2015 Jorge Gabayet, Western University (presentation)
Juliana Carneiro, Wayne State University (poster)
- 2016 Viktor J. Cibulskis, Purdue University (presentation)
Xiang-Kui Gu, Wayne State University (poster)
- 2017 Umar Aslam, University of Michigan (presentation)
Michael Cordon, Purdue University (poster)
Da Li, Wayne State University (poster)
- 2018 Phillip M. Kester, Purdue University (presentation)
Jason S. Bates, Purdue University (poster)
- 2019 Steven Chavez, University of Michigan, Ann Arbor (presentation)
Kody G. Whisnant, Wayne State University (poster)

ABSTRACTS

2021 INVITED LECTURE

SINGLE ATOM CATALYSIS: FROM AN ACADEMIC CURIOSITY TO INDUSTRIAL APPLICATIONS

Abhaya K. Datye

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University of New Mexico, Albuquerque, NM 87131, USA

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Over the past decade, single atom catalysis has evolved from being an academic curiosity to one of the most widely studied methods for the synthesis of novel catalytic materials [1]. The promise of single atom catalysts is to lower the requirements for platinum group metals by utilizing these metals more efficiently and to create novel catalytic pathways. For industrial applications, single atom catalysts need to be stable under reaction conditions and demonstrate durability during accelerated aging. Recent research shows pathways for scalable synthesis of single atom catalysts that might deliver catalysts meeting the thermal durability requirements of industry while yielding reactivity improvements over conventional supported metal nanoparticle catalysts. Since mobile single atoms constitute the dominant mechanism for catalyst sintering via Ostwald ripening, improving the stability of single atoms could help improve the durability of all heterogeneous catalysts used in industry. In this presentation we will describe recent work on an approach which we termed atom trapping [2]. Our initial work focused on trapping volatile metal oxides such as PtO₂, to improve the durability of Pt catalysts, but we are now learning how this approach can be more broadly applicable. We will describe how fundamental understanding of the stabilization of single atoms and sub-nanometer particles and clusters can be helpful in applications ranging from emission control to hydrocarbon conversion.

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PREDICTING THE STABILITY METRICS OF GENERIC NANOCATALYSTS AND THEIR UNCERTAINTIES ON-THE-FLY

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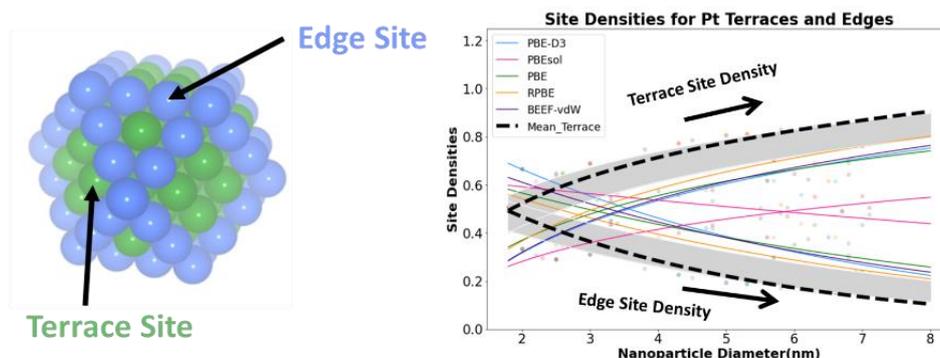
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Advances in computational catalysis have enabled predictions of reactivity metrics on nanoparticles. It is however equally important to determine nanoparticle stability metrics to bridge the materials gap between models and structures under reaction conditions. These stability metrics include nanoparticle cohesive energies, surface energies of crystal planes, and the distribution of differently coordinated metal atoms of a nanoparticle. We have developed the Alloy Stability Model which unites machine learning and physical theories to predict nanoparticle stability metrics. Our model yields errors of 0.1 eV/atom across a range of sizes (sub-nm clusters to 10 nm) and compositions (p/d block metals). Leveraging this model, we introduce a robust algorithm to predict nanoparticle stability metrics with their uncertainties. Using the Bayesian Error Estimate Functional, we generate ensembles for energies of individual metal atoms in nanoparticles. These ensembles depend on the composition and coordination numbers (CN) of nearest neighbours. We insert this ensemble into the Alloy Stability Model thus generating new ensembles for nanoparticle cohesive energies, surface energies, and Wulff constructions. The ensemble of nanoparticle cohesive energies as a function of nanoparticle diameter follows the storied Gibbs-Thomson relation, as is noted in calorimetry experiments. Ratios of surface energies between crystal planes have a low variance of ~15% due to error cancellation. This low variance results in Wulff shapes being insensitive to the density functional approximation. We examine size-dependent trends in the densities of edge (CN: 6, 7) and terrace (CN: 8, 9) within the ensemble of Wulff shapes. The densities of edge and terrace sites vary by ~ 10%. This approach to count specific active sites and their variance can assist experimentalists in computing turnover frequencies where CO/H₂ titration is challenging. Our analysis has positive implications for designing catalytic nanoparticles where precision in having high densities of specific active site ensembles is important.



ACCUMULATION AND NATURE OF A THERMODYNAMICALLY-STABLE PtO_xH_y INTERFACE ON Pt(111) DURING CA BETWEEN 0.5 AND 1.1 V_{RHE}

Arthur J. Shih^{1,2}, Kasinath Ojha¹, Mingchuan Luo¹, Xiaoting Chen¹, Zhiqin Liang¹, Matias Villalba¹, Francesc Valls Mascaró¹, Hassan Nagra¹, Rafaël Vos¹, Guangdong Liu³, Jeffrey Greeley², Zhenhua Zeng², Marc T.M. Koper¹

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²Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN, USA

³School of Physics and Electronics, Hunan University, Changsha, China

Atomic understanding of interfaces (defined as the conglomerate of metal surfaces, adsorption layer (adlayer) species, and the double layer) provides fundamental guidance toward the modeling and design catalysts with improved activity, selectivity, and stability. A comprehensive understanding on how the metal-environment interface behaves is critical for predicting, designing, and improving current commercial technologies and opening doors for the development of future technologies. For instance, fuel cells that utilize platinum typically operate between 0.6 and 1.0 V versus the reversible hydrogen electrode (V_{RHE}) (1), which is the potential range where Pt oxidation to PtOH adlayer species dominate in HClO_4 (2-4).

We present the identification and characterization of an anomalous reduction feature at $\sim 0.53 V_{\text{RHE}}$ in the cyclic voltammogram (CV, dynamic) after chronoamperometry (CA, steady-state) of Pt(111) in Ar-saturated HClO_4 in the PtOH region (0.6 to 1.1 V_{RHE}) (5,6). From a combination of electrochemical (CV), titration (CO stripping), spectroscopic (*in-situ* FTIR), and imaging (*in-situ* AFM) probes, we propose that a thermodynamically stable PtO_xH_y ($x, y = 0, 1, 2$) interface is responsible for the anomalous reduction feature at $\sim 0.53 V_{\text{RHE}}$. We also find that CA induces mild roughening of the Pt(111) surface, presumably due to an OH-induced release of surface stress. This mildly roughened Pt surface reverses to well-defined Pt(111) with the aid of hydrogen adsorption at potentials $< 0.4 V_{\text{RHE}}$. This discovery opens doors to better understand on how the Pt-electrolyte interface (such as in fuel cell technologies) responds to both dynamic and steady operating conditions.

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INVESTIGATING SURFACE AND GAS-PHASE CHEMISTRIES DURING THE BORON NITRIDE-CATALYZED OXIDATIVE DEHYDROGENATION OF PROPANE

Juan M. Venegas^{a,†}, Zisheng Zhang^b, Theodore O. Agbi^a, William P. McDermott^c, Anastassia Alexandrova^b, Ive Hermans^{a,c}

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^cDepartment of Chemistry, University of Wisconsin – Madison; Madison, WI

The exothermic oxidative dehydrogenation (ODH) of light alkanes to generate olefins has the potential to be a disruptive technology in the chemical industry. This process improves on process inefficiencies of non-oxidative dehydrogenation methods or steam cracking technologies predominantly used today. Despite decades of research on metal oxide catalyst systems, selectivity towards the desired olefin product remains low at industrially attractive conversions. As such, new catalyst systems need to minimize undesired combustion side reactions under ODH conditions.

Over the last years, we have identified boron-based materials, such as hexagonal boron nitride, as a new class of ODH catalysts.¹ These materials offer improved selectivity towards propylene during the ODH of propane and show decreased yields of combustion side products. While spectroscopic characterization has identified BO₃-type surface structures as possible active sites, the reaction mechanism that affords the unique selectivity of boron-based catalysts remains unknown. In this contribution², we combine catalytic activity measurements with quantum chemical calculations to propose that the remarkable product distribution during boron-catalyzed ODH can be rationalized by a combination of surface-mediated formation of radicals over metastable sites³ and their sequential propagation in the gas phase. Based on known radical propagation steps, we quantitatively describe the oxygen pressure-dependent relative formation of the main product propylene and by-product ethylene. The free radical intermediates are most likely what differentiates this catalytic system from less selective vanadium-based catalysts. Furthermore, this work also highlights the role of water, formed during the reaction, in modulating the reactivity of boron nitride catalysts. These investigations provide a new paradigm that considers gas phase chemistry for the design of improved ODH catalysts.

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MACHINE-LEARNING INTERPRETABLE CHEMISORPTION MODELS FOR ALLOYS

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Quantifying and understanding chemisorption on metal alloys, which is the direct chemical bonding of an atomic or molecular species to a metal surface, is central to understanding catalysis, corrosion, electrochemistry, and many other fields. Despite the fundamental nature of chemisorption, linking the structure and composition (i.e., the geometry) of different alloys to their chemisorption properties remains a crucial challenge. This talk will address two recent efforts to use machine learning to develop accurate and interpretable chemisorption models for Rh-, Pd-, Ag-, Ir-, Pt-, and Au-metal alloy surfaces subject to various strain- and ligand-induced changes to the alloys. An application of generalized additive models (iGAM models) to discovering predictive structure-property models will be discussed.[1] These iGAM models can quantify the chemisorption strength of O, OH, S, and Cl with a strong degree of predictive accuracy, with an average root-mean-square-error (RMSE) of 0.046 eV for samples in the test set, and can be interpreted to shed light on the critical geometric features of the adsorption site that impact the relative chemisorption strength. Secondly, an application of unsupervised machine learning using principal component analysis (PCA) to identify electronic-structure descriptors will be discussed.[2] The machine-learned descriptors yield more accurate chemisorption models than traditional electronic structure descriptors (e.g., the *d*-band center), yet their interpretation suggests that the physical trends they capture are entirely consistent with prior efforts to develop electronic-structure chemisorption descriptors for alloys. Ultimately, these interpretable ML approaches provide a pathway for rapidly connecting the chemisorption properties of catalysts to their geometric structure and composition.

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OXYGEN ELECTROCATALYSIS BY NON-STOICHIOMETRIC MIXED METAL OXIDES: AVENUES FOR ENGINEERING ACTIVE AND STABLE CATIONIC CENTERS

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Compositionally versatile, non-stoichiometric metal oxides belonging to the perovskite family, of the general form $A_{n+1}B_nO_{3n+1}$ ($n = 1, 2, 3 \dots \infty$; A = rare earth/alkaline earth metal; B = transition metal), have attracted vast interest for various catalytic reactions. In particular, they have been explored as catalysts for efficient electrochemical transformations of molecular oxygen (i.e., oxygen reduction and evolution reactions (ORR/OER)), which remain cornerstones for sustainable energy conversion and storage [1]. Although, the immense phase space of these oxides presents numerous opportunities to tune their catalytic performance for targeted reactions, it is limited by lack of effective design criteria. For instance, the current paradigm to describe the electrocatalytic activity of 3d transition metal-based mixed metal oxides for ORR/OER, primarily relies on the bulk electronic structure of transition metal cations in the oxide, which often fails to comprehensively describe their surface reactivity [2]. To overcome these limitations, we have combined insights from periodic density functional theory calculations and experimentally measurable surface properties of working oxides ($n=1$ A_2BO_4 and $n=\infty$ ABO_3 oxides) to develop surface electronic structure-function correlations for ORR ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$) in alkaline media [3,4]. ORR is used as a probe reaction; however, this approach can be extrapolated to other reactions. We find that the oxide surface reducibility, which is an indicator of the metal–oxygen bond strength in the oxide and can be described by the surface oxygen vacancy formation energy (E_{V_O}), captures the adsorption energetics and consequently be used to describe their electrocatalytic activity. The oxide surface reducibility is measured experimentally using H_2 -temperature programmed reduction (H_2 -TPR) and exhibits a volcano relationship with the measured electrochemical activity (Figure 1). A correlation between the surface reducibility and the stability of the oxides is also observed, making this descriptor comprehensive in describing the overall electrocatalytic performance (activity and stability) of these oxides. Extension of such descriptors to design atom efficient 4d/5d cationic centers in these oxides will also be discussed. These insights open avenues for engineering active and stable cationic centers in non-stoichiometric mixed metal oxide electrocatalysts for targeted reaction chemistries.

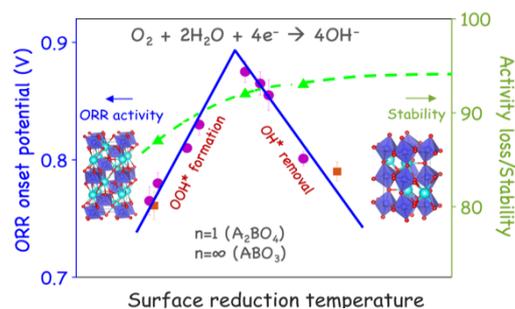


Figure 1. Volcano type relationship correlating the surface reducibility of non-stoichiometric mixed metal oxides to their electrocatalytic activity and stability.

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INFLUENCE OF ANIONS ON CHARGE TRANSFER IN REDOX COUPLES FOR FLOW BATTERIES

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Redox flow batteries (RFBs) are a promising technology to store electricity, but they suffer from high costs in part arising due to slow charge transfer kinetics, preventing their large-scale deployment. The anions in the aqueous electrolytes used in RFBs affect the structure of the reactive species in solution. Additionally, these anions influence the charge transfer process either by getting adsorbed and changing the number of available sites for reaction on the electrode surface, or changing the energy of the adsorbed intermediate. However, there is a lack of systematic study that simultaneously identifies these structures and looks at the adsorbed intermediates to understand the reaction mechanism in the presence of anions, hindering the design of novel electrolytes and electrocatalysts.

In this talk, we will discuss the influence of anions on the V^{2+}/V^{3+} redox couple by identifying the structures of vanadium ions and conducting kinetic measurements on a controlled glassy carbon surface in various acidic electrolytes ($HClO_4$, H_2SO_4 , HCl , HBr , and HI).^[1,2] We choose V^{2+}/V^{3+} because V^{2+}/V^{3+} kinetics in part limits the performance of most commercialized vanadium RFBs and the similarity in the observed kinetic enhancement in the presence of Cl^- for Cr^{2+}/Cr^{3+} , Fe^{2+}/Fe^{3+} , Cu^+/Cu^{2+} , etc. redox couples, suggesting the possible similarity in the reaction mechanism.

We show that anions influence the V^{2+}/V^{3+} kinetics by changing the energetics of the adsorbed intermediate. This is identified by the decreasing apparent activation energy with increasing adsorption energy of the $[anion-V^{3+}]$ intermediate. The apparent frequency factor follows the order opposite to the coverage of anions on glassy carbon, indicating that coverage is not responsible for the observed kinetic trends.^[1,2] We compare the trends in adsorption energy of intermediates for these other kinetically similar behaving redox couples to rationalize trends in their charge transfer.^[3] This work highlights the importance of understanding fundamental reaction mechanisms to develop low-cost energy storage technologies.

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CeO_x-Cu-BASED CATALYSTS FOR CO₂ HYDROGENATION

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There is a global concern about the increasing concentration of CO₂ in the atmosphere, as it is the leading cause of global warming. To mitigate its impact, research efforts have geared towards CO₂ capture and catalytic transformation into chemicals and fuels. CO₂ conversion to methanol is one of the most attractive routes because methanol is a raw material largely used in chemical production and it can also be used as a fuel for direct methanol fuel cells and as a hydrogen storage medium. However, the production of methanol from CO₂ is challenging due to the chemical inertness of CO₂ and the prevalence of competitive side reactions, such as methanation and reverse water-gas shift reaction.

Graciani et al. [1] found one of the most promising catalysts for the reduction of CO₂ to methanol. They found that the production of methanol was ~200 times faster with a CeO_x/Cu(111) catalyst than with Cu(111), and this was attributed to CO₂ being absorbed on Cu-ceria interfaces in the form of unstable carboxylate (CO₂^{δ-}) species that readily convert into methanol. Inspired by their findings, we synthesized a series of inverse CeO_x-Cu/SiO₂ catalysts with different CeO_x loadings to increase the number of Cu-ceria interfacial sites. These were synthesized using surface organometallic chemistry (SOMC) over a monometallic Cu/SiO₂ catalyst. Unfortunately, kinetics results showed that these catalysts were selective towards CO instead of methanol. Extensive material characterization showed that the cerium organometallic precursor was not selectively deposited onto the silica-supported Cu nanoparticles. Instead, a high fraction ended on the support forming ceria nanorods (Figure 1), thus minimizing the formation of Cu-ceria interfacial sites for methanol production.

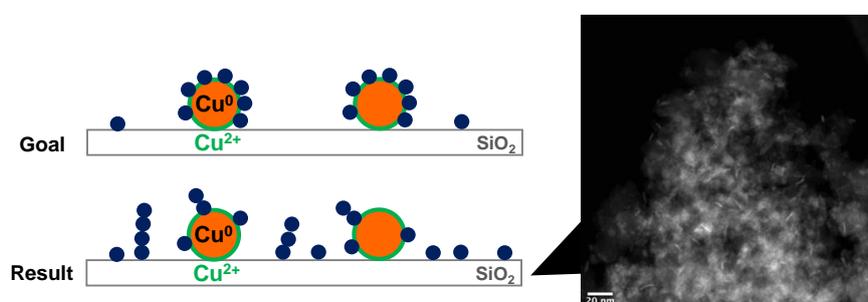


Figure 1. Inverse CeO_x-Cu/SiO₂ catalysts: goal vs resulting material (with STEM image showing the presence of ceria nanorods).

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2021 PARRAVANO AWARD LECTURE

EMBRACING THE COMPLEXITY OF HETEROGENEOUS CATALYTIC STRUCTURES: CATALYSIS BY NONSTOICHIOMETRIC MIXED METAL OXIDES AND 3-DIMENTIONALLY ENGINEERED METAL CATALYSTS

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Tuning the catalytic properties of active sites in heterogeneous catalysts for targeted reactions has been a long-standing goal in the community. In the first part of my talk, I will discuss our efforts in combining theoretical calculations, controlled synthesis, advanced characterization and testing to show that nonstoichiometric mixed metal oxides belonging to the perovskite family can be used as frameworks to tune the catalytic properties of cationic centers. This will be illustrated through their catalytic application to electrochemical reactions involving oxygen in alkaline media. We show that (i) the electronic structure of the $4d/5d$ transition metal cations can be tuned via compositional variations in the perovskite framework to achieve the outmost reactivity for the oxygen reduction reaction, and (ii) the oxide framework can be used as a platform for *in situ* generation of highly catalytically active sites for the oxygen evolution reaction.

In the second part of my talk, I will highlight our work on controlling the selectivity of supported metal catalysts by tuning their 3-dimensional environment via confinement within porous oxide shells or through surface bound ligands. As an example, I will show that tuning the functionality of ligands bound to the surface of Pd, can be used as a lever to control selectivity toward direct synthesis of H_2O_2 from molecular hydrogen and oxygen at sub-ambient temperatures.

ELECTROCATALYTIC NITRATE REDUCTION TO AMMONIA ON METALS AND ALLOYS

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Nitrate produced from industrial and agricultural processes has imbalanced the global nitrogen cycle. Electrocatalytic reduction is a promising route to remediate nitrate while generating products such as ammonia or N_2 . However, new catalysts with improved stability, activity, and selectivity are required to enable practical electrocatalytic nitrate reduction (NO_3RR). To guide catalyst design, we have studied NO_3RR on metals and alloys.

Using density functional theory (DFT) calculations and microkinetic modeling, we predicted activity and selectivity trends of transition metals for NO_3RR .^[1] The adsorption strengths of oxygen and nitrogen atoms act as descriptors for the overall activity and selectivity of electrocatalysts. Theoretical activity volcano plots, selectivity maps, and surface species coverages were predicted for transition metal electrocatalysts. The microkinetic model rationalizes several experimental observations including the activity trends of pure metals and in situ X-ray absorption spectroscopy measurements of competitive adsorption between hydrogen and nitrate on Pt/C.

Based on the volcano plots, we predicted that Pt_xRu_y alloys are promising catalysts for NO_3RR . To verify these predictions, the surface-area normalized activity of platinum-ruthenium (Pt_xRu_y/C) catalysts of different compositions for NO_3RR were measured. The Pt_xRu_y/C alloys are more active than Pt/C, with $Pt_{78}Ru_{22}/C$ six times more active than Pt/C at 0.1 V vs. RHE. DFT calculations rationalize the maximum activity observed experimentally through tuning of the nitrate and hydrogen adsorption energies with alloy composition. By experimentally confirming the use of N and O thermodynamic descriptors and theoretical volcano plot to find active alloys, these findings provide a blueprint to rationally select alloy compositions for NO_3RR .^[2]

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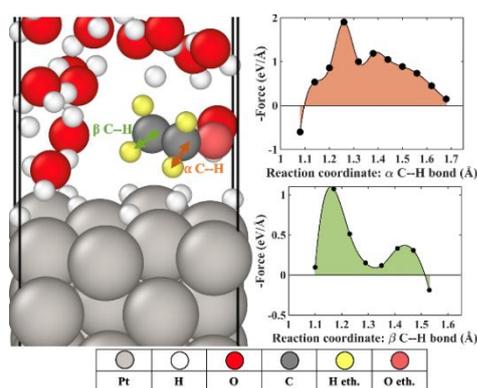
A FIRST PRINCIPLES ANALYSIS TO UNDERSTAND THE POTENTIAL DEPENDENT REACTION MECHANISM OF ETHANOL ELECTRO-OXIDATION ON Pt(100) SURFACE

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Direct ethanol-based fuel cells (DEFC) are a viable source for renewable energy production, with numerous environmentally friendly ethanol feedstocks sources, such as biomass and CO₂ reduction,^{1,2} available. Despite these advantages, DEFC's require high overpotential and suffer from low selectivity to fully oxidized product CO₂ (12 e⁻ per ethanol) on pure metal catalyst.³ To systematically understand these phenomena, and thereby facilitate design of improved DEFC's, studies have aimed to probe the fundamentals of the reaction chemistry on single crystal surfaces of noble metal catalysts such as Pt. However, the mechanistic details of the reactions are not fully known, and even basic information such as the nature of the rate-limiting step is not understood.

In this work, we consider a detailed analysis to understand the reaction mechanism of ethanol (CH₃CH₂OH) electrooxidation on Pt(100) single crystal surface in the lower (0.2-0.3 V vs. SHE) and higher (0.6-0.8 V vs. SHE) overpotential regions. To elucidate the reaction mechanism, we make use of periodic Density Function Theory calculations combined with theoretical electrochemistry analyses. We first, perform a coverage analysis, to estimate the optimal coverage of H* and OH* on the surface in the potential region of interest.⁴ Then, we elucidate the reaction mechanism by incorporating various effects such as reactant coverages and solvation, as well as by considering chemical and electrochemical reaction barriers, determined using techniques such as explicit proton transfer from water bilayers, potential of mean force simulations using ab-initio molecular dynamics, and the Climbing Image Nudged Elastic Band (CINEB) algorithm.⁵ Finally, we discuss the detailed reaction mechanism by shedding light on selectivity determining reaction steps by performing a potential dependent mechanistic analysis.



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LEVERAGING ENCAPSULATED MORPHOLOGIES TO IMPROVE CATALYTIC ACTIVITY AND DURABILITY

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Catalyst restructuring is an unavoidable phenomenon in many high-temperature applications. Unfortunately, this restructuring typically leads to the sintering of active metal and supporting domains, adversely affecting catalytic activity and the utilization of precious metal content. While several methodologies have been proposed for mitigating the processes that cause sintering, stabilizing high dispersions of active metal under periodic exposure to high temperatures during operation or maintenance remains challenging. Here we investigate how encapsulating morphologies, in which active metal domains are explicitly separated from one another through encapsulation by a porous support, can be designed to improve activity and durability in high-temperature applications.

We demonstrate that encapsulating a single palladium core in a porous ceria shell can facilitate favorable high-temperature (800°C) restructuring outcomes, which improves both activity and durability.[1] Encapsulation facilitates this favorable restructuring by providing a physical barrier that promotes the disintegration and emission of small metal species and inhibits local agglomeration through its porous, tortuous structure. As a result, active metal becomes trapped on the support in a highly dispersed fashion. The coordination between palladium and ceria that arises during the favorable restructuring improves the recruitment of lattice oxygen and, consequently, catalytic performance. This coordination also synergistically stabilizes metal and support species from agglomeration during repeated exposure to 800°C aging conditions. As such, core@shell morphologies appear to be a promising platform for promoting favorable high-temperature restructuring that improves catalytic performance, stability, and material utilization.

In applications where intermediate temperatures (550°C) are used for catalyst maintenance and regeneration, accomplishing favorable restructuring is challenging. Sintering, however, can still readily occur. We delineate a novel synthesis strategy of encapsulating and dispersing active silver nanoparticles in a porous titania shell to address this.[2] We discover that subjecting the encapsulated catalyst to a post-synthesis, solvothermal treatment step effectively anchors the silver to the support, which helps maintain superior activity under repeated aging cycles. Ultimately, we show that this combination of encapsulation and solvothermal treatment helps maintain a uniform metal particle distribution (2–5 nm) and promotes metal-support interactions by maximizing interfacial sites, which improves activity and durability. Serendipitously, we find that this generalizable synthesis approach can be used to stabilize high dispersions of active metal at temperatures as high as 800°C.

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CO₂ CAPTURE AND CONVERSION WITH DUAL-FUNCTION MATERIALS

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Extrapolations of emissions trends suggest that the CO₂ concentration in the atmosphere will reach 450 ppm before mid-century, with risk of catastrophic impacts [1]. Therefore, future strategies should focus on energy security while reducing the CO₂ emissions together with active removal. CO₂ capture and sequestration together with CO₂ capture and catalytic conversion to fuels and materials might help to mitigate the greenhouse effect. However, the latter is more desirable due to its simultaneous economic and environmental sustainability. Dual-function materials (DFMs), which are able to capture CO₂ and convert it into value-added products, might help eliminate the energy requirement, corrosion, and transportation issues associated with capture and sequestration [2]. Additionally, their use at the exhaust of combustion (e.g., flue gas at power plants) seems very attractive, not only because that would reduce the amount of gases emitted to the atmosphere, but also because industries could economically benefit from a waste. In this talk, we will summarize the progress in the field, which have been mostly geared towards the development of DFMs for CO₂ capture and methanation. Then, we will introduce the current efforts in our lab, which is focused on the controlled synthesis of DFMs for CO₂ capture and conversion into methanol: $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$ ($\Delta H_r^\circ = -49.5 \text{ kJ/mol}$). One of the advantages of this reaction is that it is exothermic, which could contribute to an efficient heat integration with the CO₂ desorption and spillover to the catalytic sites.



Figure 1. Illustration of dual-function materials for CO₂ capture and conversion [2].

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RHODIUM SINGLE-ATOM CATALYSTS ON TITANIA FOR REVERSE WATER GAS SHIFT REACTION EXPLORED BY FIRST PRINCIPLES MECHANISTIC ANALYSIS AND COMPARED TO NANOCCLUSERS

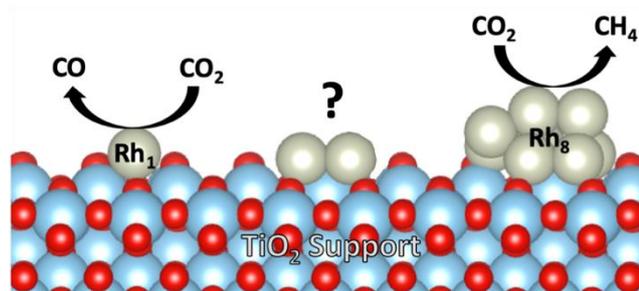
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Heterogeneous catalyst research offers promising strategies for converting CO₂ emissions into useful chemical feedstocks, providing an economic incentive for CO₂ conversion. To advance the effort for cost-effective CO₂ reduction, catalysts must be highly active and selective while minimizing the amount of precious metal required. Here, single-atom catalysts offer multiple advantages over larger nanoparticles. Single-atom catalysts are often highly active and selective due to their single-site nature and their unique electronic properties. Additionally, single-atom catalysts can achieve nearly 100% metal atom dispersion.

The thermocatalytic reduction of CO₂ by H₂ proceeds via two competing reaction mechanisms—the reverse water gas shift reaction (rWGSR, CO₂ + H₂ ⇌ CO + H₂O) and methanation (CO₂ + 4H₂ ⇌ CH₄ + 2H₂O). Single-atom Rh₁ catalysts on TiO₂ show high selectivity toward the rWGSR compared with larger Rh nanoclusters,[1] but the origin of this size-dependent selectivity has not been fully explained at an atomistic level. In this talk, we report density functional theory (DFT) calculations and mean-field microkinetic simulations that explain the high rWGSR activity of Rh₁ on anatase TiO₂ and compare Rh₁ binding characteristics to Rh nanoclusters (**Scheme 1**).²

The plausible active sites of Rh₁/TiO₂(101) were found based on DFT-computed formation energies, CO-Rh₁ vibrational frequency analysis, and microkinetic modeling. Predicted turnover frequencies and apparent activation barriers for Rh₁/TiO₂(101) at a variety of sites indicate two likely mechanisms: a fast reaction involving support oxygen vacancies, and a hydrogen-assisted mechanism involving Rh₁OH species. Rh₁/TiO₂(101) is selective toward CO rather than CH₄ because of weaker adsorption of CO, larger barrier for C-O bond dissociation, and lack of nearby metal sites for H₂ dissociation relative to nanoclusters. Ultimately, this study clarifies the origin of the higher rWGSR selectivity of Rh₁ catalysts compared with Rh nanoclusters on anatase TiO₂, and discusses strong parallels to other single-atom and nanocluster systems for rWGSR.



Scheme 1 – Single atom Rh₁ catalysts promote the reverse water gas shift reaction while clusters such as Rh₈ promote methanation. This selectivity difference between single atoms and clusters is explored using DFT calculations and microkinetic modeling.

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EXAMINING Pd SMALL-PORE ZEOLITES FOR LOW-TEMPERATURE CATALYTIC OXIDATION OF METHANE

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Methane (CH₄) is a relatively clean burning fossil fuel that generates less carbon dioxide (CO₂) than petroleum due to its high hydrogen-to-carbon ratio (H/C = 4), but it is also a potent greenhouse gas with more than 80 times the global warming potential (GWP) of CO₂ over a 20-year span when released into the environment, even in small amounts [1]. Pd/Al₂O₃ catalysts are active for CH₄ oxidation at temperatures above 550 °C under CH₄-rich (> 4%) conditions, they are unable to attain high CH₄ conversion (> 90%) at low temperatures (< 400 °C) under lean conditions, such as those encountered in the exhaust of natural gas-fired engines, due to the high air/fuel ratios.[2] However, the active Pd metal is susceptible to steam-induced sintering in the presence of water from the exhaust, thereby lowering CH₄ conversion and reducing catalyst life.

Pd-containing small-pore zeolites, such as LTA and CHA, are promising catalysts for low-temperature CH₄ oxidation due to their tunable hydrophobicity, superior thermal stability, and ability to confine active metals. For the present study, high-silica (Si/Al = 31-80) LTA and CHA (i.e., SSZ-13) were prepared through direct hydrothermal synthesis, in fluoride [3] and hydroxide media, respectively, and then post-synthetically ion-exchanged with Pd to 1 wt.%. Low-temperature CH₄ oxidation activity of Pd/H-LTA and Pd/H-SSZ-13 was evaluated before and after simulated aging after for 1 h at 650 °C under wet-lean conditions (1500 ppm CH₄, 5% O₂, 5% H₂O, Ar bal.) The temperatures required to achieve 90% CH₄ conversion (T₉₀) was for Pd/H-LTA and Pd/H-SSZ-13 ranged from 372-384 °C with Pd/H-LTA (Si/Al = 52) exhibiting the best performance. The influences of zeolite hydrophobicity (i.e., Si/Al ratio) and Pd ion-exchange on low-temperature performance and catalyst durability will be discussed.

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SYNERGIZING ATOMICALLY DISPERSED FE AND MO-NITROGEN COORDINATED ACTIVE SITES FOR EFFICIENT ELECTROCHEMICAL NITRATE REDUCTION TO AMMONIA

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Extensive global research efforts have focused on the carbon neutral synthesis of ammonia (NH₃). To date, the majority of these efforts utilize dinitrogen (N₂) as the reactive N-source. However, due to the low solubility in aqueous electrolytes, highly stable N≡N and difficulty in selectively activating N₂ over H⁺, the Faradic efficiencies (FE), yield rates and even reliable detection remain a critical challenge.¹ Recently, increasing attention has been focused on reducing a more oxidized N-species, nitrate (NO₃⁻) to NH₃. The electrochemical reduction of nitrate serves a dual function as not only a pathway to support carbon neutral NH₃ synthesis, but simultaneously as a denitrification pathway for environmentally hazardous nitrate. Although there has been increasing attention to the nitrate reduction reaction (NO₃RR) to NH₃, only very recently have the role of atomically dispersed catalysts been investigated.² The exact reaction mechanisms of the 8e⁻ transfer process over single-atom sites is not well established.³ In this talk, we demonstrate computationally and experimentally distinct nitrate reduction reaction mechanisms over Fe and Mo active sites, where Fe sites follow a direct 8e⁻ transfer path and Mo sites follow a 2e⁻ + 6e⁻ pathway. Integrating both Fe and Mo sites on a single bi-metallic catalyst, synergizes these reaction mechanisms, resulting in a FE_{NH₃} over 90%. Establishing an in-depth understanding of these distinct reaction pathways and synergizing via a cascade mechanism, demonstrates a new cascade approach to realize highly efficient nitrate reduction to NH₃.

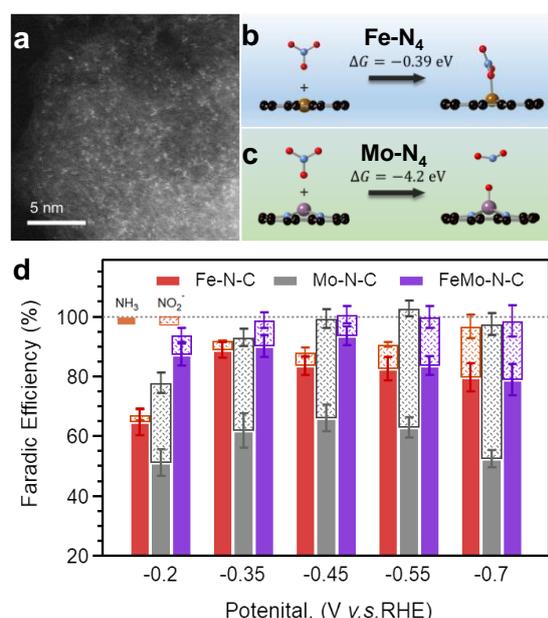


Figure 1. (a) AC-HAADF STEM image showing atomically dispersed Fe and Mo. (b) Associative adsorption of NO₃⁻ over a Fe-N₄ site (c) Dissociative adsorption of NO₃⁻ over a Mo-N₄ site (d) NO₃RR FE of NO₃⁻ and NO₂⁻ at a function of potential for the Fe/Mo/FeMo-N-C catalysts

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THE REACTION PATHWAY OF PROPANE CONVERSION TO HIGHER MOLECULAR WEIGHT HYDROCARBONS USING A PtZn/SiO₂+H-ZSM-5 BIFUNCTIONAL CATALYST

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The Cyclar process was previously developed to convert propane and butane into BTX aromatics using gallium-promoted ZSM-5 (Ga/ZSM-5). However, the yield of higher molecular weight hydrocarbons is limited by light gas formation, primarily methane and ethane^{1,2}. Relative rates and selectivity for propane conversion on two catalytic components, gallium oxide (Ga) and acidic ZSM-5 (H-ZSM-5), in the Ga/ZSM-5 catalyst suggested that methane was produced by propane monomolecular cracking on zeolites due to the imbalance of olefin rates on two catalytic functions.

A PtZn/SiO₂ catalyst, which has showed >99% propene selectivity and 100 times higher rate than Ga, was used for the dehydrogenation function. The structure of a Pt₁Zn₁ full alloy was confirmed by *in situ* x-ray absorption spectroscopy (XAS)³. The bifunctional catalysts, PtZn alloy with acidic ZSM-5 (MFI), have demonstrated high yield of higher molecular weight hydrocarbons for propane with low selectivity to methane (<5%) at ~70% propane conversion. The results suggest that light gas yield can be minimized as amount of PtZn/SiO₂ increases and ZSM-5 decreases in the catalyst. Since the olefins are much more reactive than paraffins, the rate of monomolecular cracking can be minimized but the olefin conversion rate is sufficiently high with low loading of ZSM-5. The optimal product selectivity is dependent on balance the alkane dehydrogenation and olefin conversion rate by changing the ratio of PtZn/SiO₂ and ZSM-5 in the catalyst.

The rate and selectivity of aromatics formation are higher over PtZn/SiO₂+H-ZSM-5 catalysts. The reaction pathway on a model intermediate (cyclohexene) suggests that aromatics can be formed at a higher rate and selectivity on the PtZn/SiO₂+H-ZSM-5 catalysts by the dehydrogenation pathway. This work highlights the difference in the reaction pathways for propane conversion to aromatics by ZSM-5, Ga/ZSM-5 and PtZn/SiO₂+H-ZSM-5 catalysts.

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ELECTROCATALYTIC NITRATE REDUCTION ON RHODIUM SULFIDE COMPARED TO PT AND RH IN THE PRESENCE OF CHLORIDE

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Electrocatalytic nitrate reduction (NO₃RR), where nitrate is reduced in aqueous solution on electrode surfaces, is a promising method for sustainable remediation of nitrate to value-added chemicals such as NH₃. A challenge for NO₃RR is that nitrate adsorbs weakly to many catalyst surfaces and must compete with hydrogen and reaction intermediates for active sites. This problem is exacerbated in real waste streams, where other anions such as chloride are often present (e.g., introduced via resin recovery in ion-exchange membranes) and can compete for active sites.

We report the competitive adsorption of nitrate and hydrogen and the reaction mechanism of NO₃RR. By using adsorption energies of nitrate and hydrogen as descriptors, we qualitatively understand many of the observed trends in NO₃RR activity on metal surfaces through a Langmuir-Hinshelwood reaction mechanism [1]. We show the voltage dependence of NO₃RR on platinum group metals, where competitive adsorption of hydrogen and nitrate or nitrate intermediates causes a maximum in NO₃RR activity with potential. Using cyclic voltammetry on Pt and Rh, we observe that the chloride adsorption voltage window overlaps with the maximum activity for NO₃RR, due to the related adsorption energies of nitrate and chloride. We show that even 1 mM chloride lowers NO₃RR activity by 30-60% (Figure 1), resulting from blocked sites on Pt and Rh. Using DFT, we compute the chloride and nitrate adsorption energies on a series of metals and observe linear scaling relations, such that it is unlikely any transition metal binds chloride weakly while adsorbing nitrate strongly. To address chloride poisoning, we examine rhodium sulfide (Rh_xS_y), which is an electrocatalyst with notable halide resistance. We show that Rh_xS_y is more active for NO₃RR in acidic media with and without chloride than Pt or Rh (Figure 1) and discuss plausible active sites.

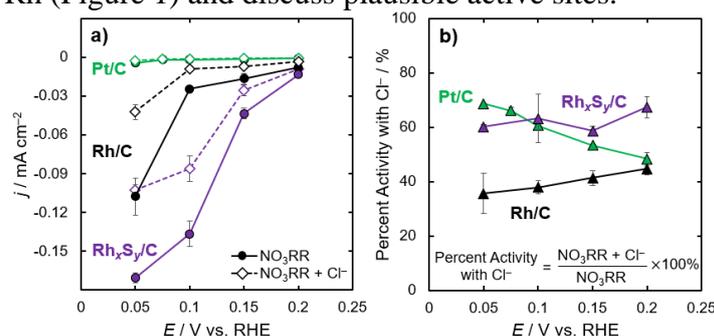


Figure 1. a) NO₃RR current density (j) on Pt/C (1 M HClO₄ + 1 M NaNO₃) and Rh/C and Rh_xS_y/C (1 M H₂SO₄ + 1 M NaNO₃) deposited on a glassy carbon rotating disk electrode at 2500 rpm rotation rate both without (filled circles) and with 1 mM Cl⁻ (open diamonds). Pt/C and Rh/C were normalized to the H_{upd} determined electrochemically active surface area (ECSA), and Rh_xS_y/C was normalized to the capacitance & XRD estimated ECSA. b) The % nitrate reduction current from the reduction currents with and without 1 mM Cl⁻ is shown for Rh/C, Pt/C, and Rh_xS_y/C for the potentials 0.05–0.2 V.

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COMPUTATIONAL INVESTIGATION AND QUANTIFICATION OF ACTIVE CU SITES IN CU-SSZ-13 ZEOLITE FOR SELECTIVE ACTIVATION OF METHANE

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Cu-exchanged zeolites have recently been found to be active for partial methane oxidation to methanol (PMO),¹ but the activities of the catalysts are very low. Further advances require a fundamental molecular-level understanding of the structure and function of the active sites to design catalysts that activate O₂ and selectively oxidize hydrocarbons. Dimeric Cu species have been proposed in literature to facilitate O₂ and CH₄ activation.^{2,3} In this project, we systematically investigate the stability and predict the quantity of Cu dimers in Cu-SSZ-13 zeolite.

Supercell density functional theory (DFT) calculations and thermodynamic analysis are applied to identify relevant species under PMO conditions. We consider the influence of local Al proximity on Cu dimer speciation, considering potential ligands (-O, -O₂, -OH) and Cu formal charges from 1+ to 3+. We find the formation of Cu dimers is highly associated with framework Al proximity. In particular, at eight-membered ring (8MR) Al pair sites, [CuOH]⁺ monomers are found to have a strong thermodynamic driving force to form O- and OH-bridged dimers, which agrees with experimental observations that SSZ-13 samples prepared to contain only [CuOH]⁺ always contain a confounding subset of O- or OH-bridged Cu dimers and/or larger aggregates⁴. We subsequently predict Cu-SSZ-13 composition phase diagrams by predicting Al distributions based on Löwenstein's rule (no Al-O-Al linkage) or rules derived from DFT calculations related to zeolite synthesis conditions⁵. Under Löwenstein's rule, we predict a significant number of Cu dimer sites that exist over Si/Al ratio 3~40. We find the number of Cu dimer sites maximizes at Si:Al around 10, which qualitatively agrees with the reported trend of methanol productivity in Cu-SSZ-13⁶. This work shows implications of finding optimal zeolite compositions and synthesis conditions for PMO reactions and eventually diversifying the strategies available to use the world's abundant hydrocarbon resources.

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UNDERSTANDING AQUEOUS-PHASE ADSORPTION AND HYDROGENATION OF PHENOL ON Pt AND Rh FROM FIRST PRINCIPLES

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Producing transportation fuels and chemicals through the valorization of biomass-derived molecules is a promising strategy to decrease our reliance on fossil fuels. Aqueous-phase thermocatalytic hydrogenation and electrocatalytic hydrogenation can be used to upgrade the mixture of organics produced from biomass pyrolysis, thus providing a route to produce CO₂-neutral chemicals from a renewable feedstock. Unfortunately, important aqueous-phase phenomena at the solvent/catalyst interface, such as the adsorption of organics, are not well understood, which makes it challenging to rationalize aqueous-phase hydrogenation kinetic trends.

In this talk, we will discuss the solvent environment's effect on the adsorption of phenol, a model bio-oil compound, and how aqueous-phase adsorption energies impact hydrogenation rates on catalytically relevant facets of Pt and Rh. We will explain how gas-phase and implicit solvent modeling techniques, which are commonly used to approximate aqueous-phase behavior, fail to reproduce experimental adsorption trends, leading to inaccurate predictions of a metal's catalytic hydrogenation activity. Specifically, these approaches predict that phenol binds over 150 kJ mol⁻¹ stronger than what is measured experimentally. Accounting for solvent displacement at the solvent/catalyst interface using a bond-additivity model based on first-principles calculations yields improved agreement with experimental measurements (Figure 1). The aqueous-phase adsorption energies of phenol on catalytically relevant facets of Pt and Rh is used to rationalize phenol hydrogenation trends, highlighting the necessity of accounting for solvent displacement at the metal interface when modeling adsorption of organic molecules in condensed-phase catalytic reactions.

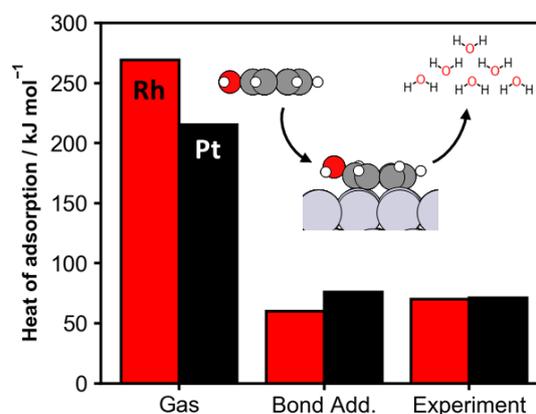


Figure 2. Heat of adsorption of phenol on Rh(111) and Pt(111) calculated using density functional theory, a bond-additivity model, and experimental measurements.

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EXAMINING ACID-BASE COOPERATIVITY IN ZEOTYPE CATALYSTS TO DIRECT CROSS-ALDOL CONDENSATION REACTIONS BETWEEN ALDEHYDES

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Molecular sieve zeotypes containing framework Lewis acid sites (e.g., M = Ti, Zr, Sn, Hf) and basic oxygen atoms have emerged as exceptional catalysts for activating carbonyl-containing molecules, such as aldehydes,¹⁻⁴ to direct carbon-carbon bond formation through aldol condensation pathways in liquid media. The acid-base pairs within Si-O-M ensembles function cooperatively in conjunction with weaker van der Waals interactions in the neighboring zeotype void environment to catalyze cross-aldol condensation reactions between aldehydes lacking α -C-H bonds and enolizable substrates. For this investigation, the cross-aldol condensation between benzaldehyde and propanal was used as a probe reaction to examine the influence of acid-base cooperative interactions and confinement effects on apparent rate constants, activation energies, initial site time yields (STY), and product selectivities toward α -methyl cinnamaldehyde (α -MCA), the cross-condensation product, and 2-methyl-2-pentenal, (2M2P), the self-condensation product. Kinetic studies were performed in a batch reactor between 363-393 K at contact times ranging from 0-48 h over medium-pore MFI (10-MR), large-pore *BEA (12-MR) and extra-large pore UTL (14-MR) zeotypes containing isomorphously substituted Ti, Zr, Sn and Hf heteroatoms.

Experimental evidence revealed trends in catalytic performance of the Lewis acid metal centers (Zr ~ Hf > Sn > Ti) for cross-aldol condensation based on initial STYs (mol α -MCA (mol M)⁻¹ h⁻¹), product selectivities, and apparent rate constants (k_{app}). Zr- and Hf-*BEA exhibited ~30-40 \times higher initial STY and ~5-7 \times higher k_{app} at 393 K than Ti-*BEA, and Ti-MFI showed the highest α -MCA selectivity among all the tested zeotypes. Additionally, extra-large pore Ti-UTL exhibited initial STY and k_{app} that were ~2-9 \times and ~1.4~1.8 \times greater, respectively, than those for Ti-MFI and Ti-*BEA. These results suggest that both the functional Lewis acid strength of the metal heteroatom and surrounding void environment contribute to the observed catalytic performance for cross-aldol condensation between enolizable aldehydes and those lacking α -hydrogens.

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CONSEQUENCES OF AND MODELS FOR INCORPORATING COVERAGE-DEPENDENCE INTO MICROKINETIC MODELS

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Adsorbates at metal surfaces interact with one another in a way that modifies adsorption energies and reaction rates.^{1,2,3,4,5} Microkinetic models used for screening metal catalysts commonly neglect these interactions because they tend not to have a strong influence on volcano maxima. Coverage dependence becomes more important when the goal becomes the prediction of product selectivity or of recovering rates, rate orders, and apparent activation energies at a higher level of fidelity appropriate for comparing with experiment.

In this work, we probe the consequences of adsorbate-adsorbate interactions within a simplified two-step reaction network inspired by ammonia synthesis and NO oxidation. We examine how rates, rate orders, apparent activation energies, and Sabatier plots respond to increasing inclusion of explicit lateral adsorbate interactions using a lattice-based kinetic Monte Carlo (kMC) framework. We subsequently extract lessons from those models and develop paradigms for incorporating coverage in a more robust way into mean-field microkinetic models.

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SYNTHESIS AND INTRINSIC ELECTROCATALYTIC ACTIVITY EVALUATION OF $\text{Ni}_{2-x}\text{Rh}_x\text{P}$ NANOPARTICLES FOR WATER SPLITTING REACTIONS IN BASIC MEDIA

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Hydrogen is an abundant energy carrier and a key element in the development of clean and renewable energy production. Water electrolysis represents a promising approach to distributed hydrogen production, but suffers from low efficiency due to the slow kinetics of the oxygen evolution reaction (OER), which is the rate-limiting step and the source of electrons for the hydrogen evolution reaction (HER). Even though noble metals such as Ru, Ir, and Pt show high electrocatalytic activity and stability toward the water splitting process, their expense precludes their large-scale adoption. One approach to optimizing the performance-cost trade-off is to dilute the noble metal with non-metals and/or base metals and exploit structure/electronic levers to maintain, or even augment, the overall activity while minimizing the amount of precious metal employed.

Recently, transition metal phosphides (TMPs) have emerged as promising catalysts for HER and OER processes. Earth-abundant phosphides of Cu, Ni, Co, Fe, Mn and combinations thereof have good activity and reasonable stabilities, with the best activities logged for bimetallic systems, although these do not reliably out-perform the state-of-the-art noble metal catalysts. Rh_2P , on the other hand, does outperform Pt for HER. In our previous work, we showed that $\text{Co}_{2-x}\text{Rh}_x\text{P}$ solid solutions exhibit enhanced activity for HER and OER relative to the end-members, with Co-rich phases optimal for OER and Rh-rich phases optimal for HER. Thus, diluting a noble metal with a base metal makes it possible to achieve highly active, comparatively low-cost TMPs for catalytic applications.¹⁻³ In the present contribution, we seek to understand how different base metals affect the activity of bimetallic TMPs based on Rh, focusing on $\text{Ni}_{2-x}\text{Rh}_x\text{P}$. The synthesis of discrete nanoparticles of $\text{Ni}_{2-x}\text{Rh}_x\text{P}$ and their composition-dependent efficacy for water electrolysis will be described and discussed in the context of intrinsic activities assessed through electrochemical surface area measurements.

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