

The Catalysis Club of Philadelphia

(In Person) Thursday, October 19th, 2023

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Active site requirements for chemoselective hydrogenation with binary and ternary intermetallics

Speaker: Prof. Robert Rioux

Pennsylvania State University

Understanding the role of corrosion and reactive oxygen species in electrochemical ozone production

Student Speaker: Rayan Alaufey

Drexel University

Meeting Agenda:

Social Hour 5:30 PM
Dinner 6:30 PM
Meeting 7:30 PM

Meeting Registration:

Members: \$45.00
Non-Members: \$55.00
Stud. & Retired Members: \$35.00

Please register online for this In-person meeting by **Thursday, October 12th** at [CCP website](#).

Meal Selection (Included):

Please make one selection for your dinner (included in registration) when you sign-up for the meeting from the following options:

1. Entrée & Dessert— Maryland Crab Cakes; Tiramisu

2. Entrée & Dessert— Sliced Roast Sirloin; Tiramisu
3. Entrée & Dessert— Eggplant Parmesan (*vegetarian*); Tiramisu
4. Entrée & Dessert— Cavatappi Pasta (*vegan*); Fruit Cup

Salad comes with any option: Caesar Salad

Membership Registration:

Membership dues for CCP 2023-24 meeting season will be \$25 (\$5 for the local chapter and \$20 for the national club). Dues for students, post-docs and retirees will be \$10 (\$5 for the local club and \$5 for the national club). Please sign-up membership ([Link](#)) for more benefits on meeting registrations and networking events!

Please contact our Treasurer Steve Hardwick (sjh.wilm.de@gmail.com) or Chair Angela Zheng (angela.zheng@matthey.com) if you need any assistance.

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Prof. Robert (Rob) M Rioux

Active site requirements for chemoselective hydrogenation with binary and ternary intermetallics

Department of Chemical Engineering and Chemistry, Pennsylvania State University

Abstract: A reliable method to design site-isolated catalysts is through the synthesis of intermetallic bulk compounds where a small number of active atoms are isolated in an inert matrix of a second metal. Intermetallics – multi-metal systems with a well-defined arrangement of the metal atom – offer a platform to control active site structure and composition [1]. They represent an ideal model system for studying structure-function relations in metal-catalyzed hydrogenation reactions. The Pd-(M)-Zn γ -brass phase (M = Zn, Pd, Cu, Ag, Au) is uniquely suited for the controlled synthesis of Pd-M-Pd active ensembles with controlled nuclearity and composition isolated in a Zn matrix. The prototypical Pd₈Zn₄₄ structure contains only isolated Pd atoms, but with increasing Pd concentration by Zn substitution (Pd_{8+x}Zn_{44-x}, x = 0-2) within the bounds of the γ -phase, a fixed number of Pd-Pd-Pd trimers form in the bulk. These multi-atomic heteronuclear active sites are catalytically distinct from Pd single atoms, fully coordinated Pd and within the Pd-M-Pd series. With these catalysts, we quantify the unexpectedly large effect of active site nuclearity for acetylene semi-hydrogenation in an ethylene and hydrogen rich environment. The trimer-containing Pd₉Zn₄₃ and Pd₁₀Zn₄₂ have $\sim 10^6$ times higher activity compared to trimer-free Pd₈Zn₄₄, but the latter leads to net ethylene gain by only semi-hydrogenating acetylene, consistent with theoretical predictions. Pd₂M trimers demonstrate activity and selectivity intermediate to the monomer- and trimer-containing surfaces. Experimental trends show strong agreement with density functional theory (DFT) calculations, evidencing our ability to control the nuclearity and composition of active sites in intermetallics [2].

We further demonstrate the well-defined active site afforded by the γ -brass phase allows for the development of kinetic models that accurately describe apparent activation energies and reaction orders for ethylene hydrogenation on γ -brass Pd-(M)-Zn. Previous studies of the kinetics of ethylene hydrogenation on late transition metal surfaces have required the use of a “special” site on which H can adsorb without competition from ethylene within a Langmuir-Hinshelwood framework. The molecular level definition of such sites is elusive, arising from the complex combination of mixed coverages and differences in adsorbate size between ethylene and hydrogen. The isolation of Pd₁ and Pd₃ sites allows us to provide a precise definition of all possible ethylene-hydrogen co-adsorption structures and hydrogenation reaction paths, enabling a precise

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definition of site requirements. We demonstrate the high sensitivity of the H₂ reaction order on monomer- and trimer-containing Pd₉Zn₄₃ surfaces is due to the significant influence of Pd monomers on the degree of rate control due to the competitive hydrogenation of ethylene and hydrogen on the monomers. This sensitivity disappears on trimer-only containing Pd₁₀Zn₄₂ surfaces. Microkinetic modeling predicts an ethylene reaction order close to zero and hydrogen order of unity, in agreement with experimental results.

¹A. Dasgupta, R. M. Rioux. *Catalysis Today* 330 (2019) 2-15.

²A Dasgupta, H. He, R. Gong, S. -L. Shang, E. K. Zimmerer, R. J. Meyer, Z. -K. Liu, M. J. Janik, R. M. Rioux. *Nature Chemistry* 14 (2022) 523-529

³H. He, G. Canning, A. Dasgupta, A. Nguyen, R. J. Meyer, R. M. Rioux, M. J. Janik. *Nature Catalysis*. 6 (2023) 596-605.

Speaker Bio:

Robert (Rob) M Rioux is the Friedrich G. Helfferich Professor of Chemical Engineering and Professor of Chemistry at the Pennsylvania State University. Prior to joining the Pennsylvania State University in 2008, he was a National Institutes of Health Postdoctoral Fellow at Harvard University in the Department of Chemistry and Chemical Biology. He received his Ph.D. in physical chemistry from the University of California, Berkeley in 2006. He holds a B.S. and M.S. degree in chemical engineering from Worcester Polytechnic Institute and the Pennsylvania State University, respectively. He has received a number of awards, including a DARPA Young Faculty Award, an Air Force Office of Scientific Research Young Investigator Program Award, a NSF CAREER Award and a 3M Non-Tenured Faculty Award. At Penn. State, he has been recognized for his research (Pennsylvania State Engineering Alumni Society (PSEAS) Outstanding Research Award, 2014), teaching (PSEAS Outstanding Teaching Award, 2018) and advising (Pennsylvania State University Excellence in Advising Award, 2014) achievements. His group's current research focuses on the development of spatially- and temporally-resolved spectroscopic techniques for imaging catalytic chemistry, elucidation of reaction mechanisms in nanoscale systems, and the development of solution calorimetric techniques to understand catalytic processes at the solid-liquid interface.

Understanding the role of corrosion and reactive oxygen species in electrochemical ozone production



Rayan Alaufey

Advisor: Prof. Maureen Tang, Drexel university

Six-electron water oxidation, or electrochemical ozone production (EOP), offers applications for value-added electrochemical oxidations and fundamental questions about catalytic selectivity. Nickel and antimony-doped tin oxide (Ni/Sb-SnO₂, NATO) is known to be active for EOP but the mechanism of its selectivity and activity, as well as the origin of its instability is not yet clear. We combine electrochemistry, spectroscopic detection of reactive oxygen species (ROS), oxygen anion chemical ionization mass spectrometry (CIMS), and density-functional theory (DFT) simulations to identify the reaction mechanism and investigate the role of corrosion in EOP on NATO electrodes. Comparing experimental potentials with theoretical predictions indicates that hydrogen peroxide is a critical reaction intermediate. Our results suggest that the presence of nickel in NATO enables the catalysis of hydrogen peroxide to hydroperoxyl radicals, which subsequently undergo oxidation to produce ozone. Analyzing the isotopic make up of products shows that water is the primary source of ozone, but it contains oxygen that derives both from water and the metal oxide lattice. The change in the isotopic generation pattern over time suggests NATO catalysts corrode irreversibly and the lattice oxygen is not regenerated, explaining the lack of electrode stability. Further analysis of possible corrosion reactions suggests that tin oxide might corrode to generate hydrogen peroxide and tin(IV) hydroxide. The implications of this study point to fundamental technological limitations for water purification and other electrochemical advanced oxidation processes.

Speaker Bio

Rayan Alaufey is a 3rd year Ph.D. candidate in the department of Chemical and Biological Engineering at Drexel university. He is advised by Professor Maureen Tang. He earned his B.S. in Chemical engineering from the University of Rochester and his M.S. in Chemical engineering from Columbia University. Rayan focuses on investigating oxidation reactions at high potentials on inert electrodes, which encompass areas such as electrochemical ozone production and the generation of radicals on doped tin oxide catalysts. His research primarily centers on exploring the influence of catalyst structure and morphology on the underlying mechanisms of these reactions.