



## UPDATE

August 2019



*Roger Rousseau and Mike Elliott*

### **DIRECTORS' UPDATE: MOVING TOWARD MIXTURES**

PNNL's Chemical Transformations Initiative (CTI) is developing the fundamental and applied science that will integrate carbon waste management, chemical and fuel production, and the resilient 21st-century electric grid. To achieve this aspiration, CTI is laying the foundation for electrochemical conversions at low temperature in complex mixtures. We have made great strides in controlling and enhancing reaction rates for well-defined model compounds in aqueous environments, and we have also gained new fundamental insights into mixtures.

CTI is moving beyond single-component reaction mixtures by increasing our knowledge of how the chemical complexity of real feeds impacts low-temperature electrocatalytic transformations. In this quarterly update, we discuss our latest findings about the synergistic kinetics of co-conversion of phenols and aldehydes, as well as our efforts to build zeolite-based acid catalysts that will work under reaction conditions similar to electrocatalytic hydrogenation. Also in this update, we report on how multiscale modeling can account for changes in reduction rate with variations in solvent composition.

*Roger Rousseau, CTI Director*

*Mike Elliott, CTI Deputy Director*

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*Cross-disciplinary collaboration powers CTI research: Theorist Malsoon Lee and fundamental electrochemist Oliver Gutiérrez discuss the reactivity of co-adsorbed phenol and benzaldehyde.*

## PROJECT UPDATE: ENHANCING RATES THROUGH MECHANISTIC INSIGHTS

To bridge CTI's fundamental research with application, we must understand how reaction parameters and increasing complexity of the reaction media impact the performance of electrocatalysts and the kinetics of reactions.

The fundamental and applied hydrogenation teams have taken on the challenge of determining kinetic parameters, often overlooked in traditional electrochemical synthesis, and are using them to draw guidelines for catalyst and process optimization. From the fundamental perspective, we have shown increases in conversion rates by orders of magnitude.

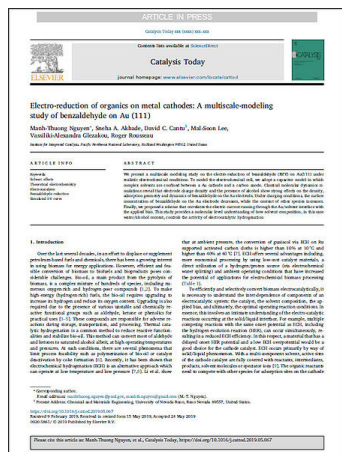
To achieve these increases, we have minimized the Ohmic drop between electrodes ([Song et al. 2016](#)), counteracted the rollover of hydrogenation rates due to excessive dehydrogenation of adsorbates ([Singh et al. 2016](#)), and studied the effects of hydronium ion concentration on hydrogenation ([Singh et al. 2019](#)). We have also optimized the particle size of metals to maximize rates ([Sanyal et al. 2018](#)) and suppressed H<sub>2</sub> evolution during hydrogenation on Pd ([Song et al. 2018](#)). Aiming at understanding electrocatalysis in mixtures, we have recently found that the rates of carbonyl hydrogenation (like in benzaldehyde) are enhanced by the co-adsorption of a second organic compound (e.g., phenol and benzoic acid) that is able to form a hydrogen bond with the carbonyl group. This rate enhancement does not occur if the hydrogenation occurs via thermal catalysis with molecular H<sub>2</sub>. We propose that there are intermolecular interactions in mixtures that may offer alternative reaction pathways. These routes, however, are activated when e<sup>-</sup>/H<sup>+</sup> pairs drive the reduction rather than H<sub>2</sub>. The team is currently testing this hypothesis following our trademark approach of combining kinetics, theory, physicochemical, and electrochemical characterizations.



## SPOTLIGHT ON STAFF: HUAMIN WANG

Huamin leads CTI's acid-base catalysis team and is making integral contributions to fundamental understanding of the reaction mechanisms, active site, and environmental requirements for dehydration reactions over zeolite catalysts. These reactions are critical to CTI for eliminating oxygen from the complex alcohol mixture after

electrocatalytic hydrogenation of biomass liquefaction oils. His team specifically developed insight into the effect of water content and structure of alcohols on the dehydration rates over acid sites in zeolite confinement (M. Shetty, F. Chen, D. Camaioni, O. Y. Gutierrez, [H. Wang](#), J. A. Lercher, Enthalpy-Entropy Compensation Effects During Hydronium-Ion-Catalyzed Elimination of Aliphatic Alcohols, in prep.). Additionally, they developed an approach to improve stability of zeolites in condensed water ([Prodinger et al. 2018](#)). Along with his work on CTI, Huamin leads several BETO-funded projects focused on upgrading biomass liquefaction oils, catalytic fast pyrolysis, and catalyst deactivation mitigation for biomass conversion. He contributes to PNNL's core BES Catalysis Program by providing an understanding of atomic-level structure/function relationships of transition metal oxide catalysts in dehydration and C-C coupling of oxygenates ([Shi et al. 2018](#); [Zacher et al. 2019](#); [Griffin et al. 2018](#)).



## CTI IN THE LITERATURE

The CTI theory team has published a first-of-its-kind work that appears as an invited paper in *Catalysis Today* and focuses on the electrochemical processes of organics under realistic conditions ([Nguyen 2019](#)). Led by Manh-Thuong Nguyen and Vanda Glezakou, this work shows how choice of solvent environment can be as critical as choice of catalysts for optimizing rates. Using scanning tunneling spectroscopy theory and molecular dynamics simulations, the team found that the simulated current density in the electroreduction of benzaldehyde on Au resembles the Butler–Volmer equation. Adding alcohols to the solvent increases the benzaldehyde population at the electrode, but decreases the current density, which is related to the organics' adsorption geometry.

## CTI HAPPENINGS

- CTI's Yuyan Shao from PNNL was invited to co-edit a [special, themed issue of \*Advanced Materials\*](#) focused on "Materials Electrochemistry for Chemical Transformation." The issue was published online on July 31, 2019, followed by print publication in early August.
- CTI will have a major presence at the ACS Fall 2019 National Meeting and Exposition in San Diego, CA. Vanda Glezakou, Yuyan Shao, Huamin Wang, and Robert Weber will be organizing four symposia in Catalysis, Energy and Fuels, and Computational Chemistry sections with topics ranging from biomass conversion to electrocatalysis. In addition, Oliver Gutiérrez, Roger Rousseau, Yuyan Shao, and Robert Weber will be giving 6 invited talks on CTI research.

- At the 2019 meeting of the North American Catalysis Society this June in Chicago, PNNL's Jamie Holladay, Abhi Karkamkar, Oliver Gutiérrez, and Huamin Wang gave talks on the the CTI teams they lead.

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## CTI BY THE NUMBERS

**2017–2020** Initiative Duration

**\$9M+** PNNL Investment

### **OUR TEAM**

**41** Staff

**18** Postgraduates

**9** New Hires

### **PRODUCTS**

**1** Invention Disclosure

**29** Journal Articles

### **RESEARCH PARTNERS**

Technische Universität München

University of Washington

University of Michigan

Oregon State University

University of Illinois, Urbana-Champaign

### **ABOUT CTI**

CTI focuses on developing catalytic science for intensified, scalable, distributed conversion of dispersed carbon into chemicals and energy-dense fuels. To meet this challenge, CTI leverages PNNL's basic and applied science teams, employing a multidisciplinary approach to develop new capabilities at PNNL to meet the needs of the future waste-to-energy economy.



[Pacific Northwest National Laboratory](#) draws on signature capabilities in chemistry, earth sciences, and data analytics to advance scientific discovery and create solutions to the nation's toughest challenges in energy resiliency and national security. Founded in 1965, PNNL is operated by Battelle for the U.S. Department of Energy's [Office of Science](#). DOE's Office of Science is the single largest supporter of basic research in the physical sciences in the United States and is working to address some of the most pressing challenges of our time. For more information, visit [PNNL's News Center](#). Follow us on [Facebook](#), [Instagram](#), [LinkedIn](#) and [Twitter](#).

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