PNNL

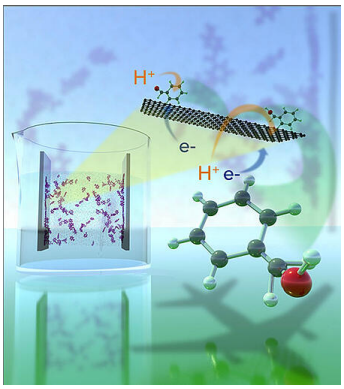
CHEMICAL TRANSFORMATIONS INITIATIVE

UPDATE

DIRECTOR'S UPDATE

CTI is making excellent progress establishing the science for the efficient electrochemical conversion of underutilized carbon resources into fuels. By integrating fundamental and applied sciences, we are discovering novel phenomena at solid-liquid interfaces, new chemical reactions, and new catalysts to enable low temperature and pressure conversion of these resources. We are increasing our understanding of how complex interfaces arise between solid electrocatalysts under an external electrochemical bias and how mixtures of liquid water and organics affect the activity and selectivity of the catalyzed reactions. And we are incorporating this growing understanding into novel reactors and process designs.

In this CTI quarterly update, we highlight how the CTI team is working toward understanding and controlling electrocatalytic hydrogenation of oxygenated organic compounds. We show how theory and computation—coupled with careful thermodynamic/kinetic measurements and in situ spectroscopy—enable us to understand the mechanisms of electrocatalytic hydrogenation. This understanding ultimately enables us to control the activity, selectivity, and electrochemical efficiency of these conversions and allows us to design better reactors and processes, moving us closer to implementation.



Theory and modeling help us understand how organics are transformed at electrode interfaces.

PROJECT UPDATE: THEORY

To predict electrocatalytic kinetics, we must understand how mass and charge move in and out of the electrochemical double layer and interact on the electrode surface. This requires simulations that are at the forefront of what can be achieved using state-of-the-art computing, involving processes occurring simultaneously on time scales ranging from picoseconds to seconds and length scales spanning nanometers to micrometers.

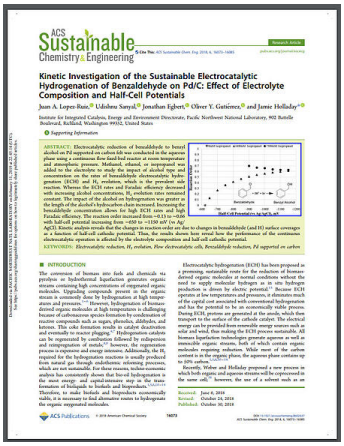
The CTI Theory Team has developed a multiscale model that includes quantum mechanical calculations to understand chemical reactivity, molecular dynamics to understand electrical double layers, and electron transfer theory to predict rates (Cantu et al. 2018; Singh et al. 2018; Yang et al. 2018; Gutiérrez et al. 2018). Working closely with the CTI experimentalists, we have begun to validate many of the discoveries from this model. These include the competition between hydrogen and organics for access to the surface of the electrocatalyst (Cantu et al. 2018; Singh et al. 2018) and the role of solvents (Cantu et al. 2018; Yang et al. 2018) and pH (Gutiérrez et al. 2018) in controlling the catalysis. We find that although simple thermodynamics models based on static calculations are good for predicting relative overpotentials of electrocatalytic reactions, we need to explicitly account for solvent and double layer effects to understand reaction rates.

Transferring this knowledge toward the conversion of realistic feeds—such as hydrothermal liquefaction oils—requires that the models address an even higher level of complexity. As such, the team is currently moving forward to understand how to contend with multicomponent solvent mixtures and competition between adsorbates.

SPOTLIGHT ON STAFF: OLIVER GUTIÉRREZ TINOCO

Oliver is one of CTI's most active early career researchers. He has played a central role in the experimental activities of the initiative, leading and making integral contributions to the fundamental research by understanding catalytic mechanisms and their impacts on catalyst design. A series of five 2018 publications illustrate his key role. These published works cover the broad research landscape targeted by CTI, from the principal chemistry (Song et al. 2018; Sanyal et al. 2018a) to catalyst characterization (Singh et al. 2018) to strategies for catalyst and process development (Lopez-Ruiz et al. 2018; Sanyal et al. 2018b). Oliver has bridged electrochemistry and heterogenous

catalysis to advance our understanding of both disciplines and to enable CTI to optimize catalysts and reaction conditions for electrochemical hydrogenation.


ACS Sustainable Chemistry & Engineering

Kinetic Investigation of the Sustainable Electrocatalytic Hydrogenation of Benzaldehyde on Pd/C: Effect of Electrolyte Composition and Half-Cell Potentials

CTI IN THE LITERATURE

The CTI Applied Electrocatalysis team, led by Jamie Holladay, recently published a systematic study of the effects of co-solvents on electrocatalytic performance, a key step towards understanding coprocessing aqueous and organic phases of liquefied biomass in the same reactor. Featured in *ACS Sustainable Chemistry & Engineering*, the team evaluated the effects of alcohols on electrocatalytic reduction of benzaldehyde with a carbon-supported palladium catalyst. The inclusion of the co-solvents allowed higher concentrations of reactants, increasing the reaction rate and Faradaic efficiency. Surprisingly, their data support a proton-coupled electron transfer reaction mechanism with Eley–Rideal first order reaction kinetics, which is a significant departure from the Langmuir–Hinshelwood mechanism that is commonly assumed.

CTI HAPPENINGS

- CTI's Yuyan Shao from PNNL is co-organizing a four-day symposium, "Sustainable Energy Conversion via Innovative Electrocatalysis and Photocatalysis," at the 2019 ACS National Meeting & Exposition. CTI staff comprise 7 of the 40 invited speakers on topics ranging from liquid fuels from biomass to new concepts for energy conversion and fuel utilization.
- CTI's Robert (Bob) Weber from PNNL was recently appointed as both a Fulbright Specialist *and* as a member of the Editorial Advisory Boards of ACS Omega and AIChE's Journal of Advanced Manufacturing and Processing.
- Johannes Lercher, CTI's Chief Scientist, was elected to the prestigious U.S. National Academy of Inventors in December 2018. He will be formally inducted in a ceremony at Space Center Houston, April 10–11.

CTI BY THE NUMBERS

2017–2020 Initiative Duration

$12M+ PNNL Investment

OUR TEAM

30 Staff

11 Postgraduates

5 New Hires

PRODUCTS

1 Invention Disclosure

27 Journal Articles

RESEARCH PARTNERS

Technische Universitäte München

University of Washington

University of Michigan

Oregon State University

University of Illinois, Urbana-Champaign

Washington State University

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

Pacific Northwest National Laboratory is the nation's premier laboratory for scientific discovery in chemistry, earth sciences, and data analytics and for 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 the PNNL's News Center. Follow us on Facebook, Google+, Instagram, LinkedIn and Twitter.

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