

# Catalysis Center for Energy Innovation GUEST SEMINAR SPEAKER

Friday, June 16, 2017

10:00 AM • 322 ISE Lab



**Professor David W. Flaherty**

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**Biography:** David Flaherty is a Dow Chemical Company Faculty Scholar and Assistant Professor of Chemical and Biomolecular Engineering at the University of Illinois, Urbana-Champaign. He earned his B.S. in chemical engineering from the University of California at Berkeley and his Ph.D. in chemical engineering from the University of Texas at Austin with Buddie Mullins. He was a postdoctoral scholar at the University of California, Berkeley with Prof. Enrique Iglesia. In 2012 he joined the faculty at the University of Illinois, Urbana-Champaign. His group applies kinetic and spectroscopic methods to study the design of catalysts and mechanisms of reactions for the production and use of environmentally benign oxidants and the conversion of small biomass-derived species in to more valuable chemicals and fuels. Prof. Flaherty is the recipient of a CAREER Award from the National Science Foundation and a Doctoral New Investigator Award from the ACS Petroleum Research Fund. Additionally, he has been named four times to the UIUC “List of Teacher’s Ranked as Excellent” and received the School of Chemical Sciences Excellence in Teaching Award in 2015.

## “Eliminating Needless Chlorine in the Production of Chemicals - Direct Synthesis of H<sub>2</sub>O<sub>2</sub> and “Green” Epoxidations”

**Abstract:** H<sub>2</sub>O<sub>2</sub> is an environmentally-benign and selective oxidant useful for epoxidations and bleaching, yet, its use is limited because the anthraquinone oxidation process is viable only at very large scales. Currently, many oxidation processes use chlorine-based oxidants (Cl<sub>2</sub>, HOCl) at a global rate of 63·10<sup>9</sup> kg Cl yr<sup>-1</sup>. Within the United States roughly 60% of chlorine is used as an oxidant in processes where chlorine does not appear in the final products (e.g., production of propylene oxide). The direct synthesis of H<sub>2</sub>O<sub>2</sub> (H<sub>2</sub> + O<sub>2</sub> → H<sub>2</sub>O<sub>2</sub>) could enable H<sub>2</sub>O<sub>2</sub> to be produced cost-effectively on-site, and even *in situ*, which would curtail needless use of chlorine, and in turn, decrease environmental chlorine pollution. This seminar will describe findings based on kinetic and *in situ* spectroscopic measurements that reveal mechanisms, active intermediates, site requirements, and functional descriptors for the formation of H<sub>2</sub>O<sub>2</sub> and its use in epoxidations.

First, direct synthesis of H<sub>2</sub>O<sub>2</sub> involves chemistry at the solid-liquid interface between the complex “broths” needed for high selectivities and supported monometallic (Pd) or bimetallic clusters. We have shown that the selectivities of H<sub>2</sub>O<sub>2</sub> formation in these systems are determined by competition between unexpected proton-electron transfer processes that form H<sub>2</sub>O<sub>2</sub> and homolytic surface reactions that cleave O-O bonds to produce water. The rates of these two pathways differ dramatically in their sensitivity on the composition of the solvent and the catalyst surface, which provides opportunities for developing highly selective catalysts.

Second, transition metal substituted zeolites efficiently catalyze the epoxidation of olefins with H<sub>2</sub>O<sub>2</sub>. Here, we demonstrate that the identities and reactivities of the oxidizing surface species that form (i.e., -OOH or -O<sub>2</sub>) upon irreversible activation of H<sub>2</sub>O<sub>2</sub> on these catalysts depend on the identity and intrinsic properties of the metal substituents. Specifically, the acid strength of the metal center is critical, and sites that provide greater functional acid strengths present lower barriers for both epoxidation reactions. Among only Group IV and V transition metals, these differences lead to epoxidation rates that vary by five-orders of magnitude and which are accompanied by a concomitant 100-fold increase in selectivities as well.

In ongoing work, we aim to develop guiding principles and reactivity/selectivity descriptors for the design of metallic catalysts for the direct synthesis of H<sub>2</sub>O<sub>2</sub> and subsequent selective oxidations by peroxo and superoxo intermediates. Ultimately, the integration of these reactions may enable new processes and clean chemistry for the oxidative functionalization of small molecules. We gratefully acknowledge support from a CAREER Award from the National Science Foundation and the Army Research Office.

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