**“Eliminating Needless Chlorine in the Production of Chemicals - Direct Synthesis of H2O2 and “Green” Epoxidations”**

Abstract: H2O2 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 (Cl2, HOCl) at a global rate of 63·10⁹ kg Cl yr⁻¹. 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 H2O2 (H₂ + O₂ → H₂O₂) could enable H₂O₂ 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 H₂O₂ and its use in epoxidations.

First, direct synthesis of H₂O₂ 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 H₂O₂ formation in these systems are determined by competition between unexpected proton-electron transfer processes that form H₃O₂ 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 H₂O₂. Here, we demonstrate that the identities and reactivities of the oxidizing surface species that form (i.e., -OOH or -O₂) upon irreversible activation of H₂O₂ 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 H₂O₂ 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.

www.efrc.udel.edu

The Catalysis Center for Energy Innovation is an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science.