Chemical & Biological Engineering Seminar

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Catalysis Beyond the Active Site

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Rates and selectivities of catalytic processes are typically considered to be prescribed by process parameters such as reactant pressures and temperature, and the identity and local structure of the active site. Secondary effects of confining voids or of adsorbed promoters are elided in such descriptions. In this talk, I will give examples of such secondary effects playing a deterministic role in the observed rates of aqueous phase isomerization of glucose to fructose over microporous Lewis acids and in the observed selectivity of epoxidation of ethylene to ethylene oxide over a promoted silver catalyst. In the first example, variations in the polarity of microporous voids that host Lewis acidic Sn sites result in ~45x higher first order rate constants (per active site, 373 K) over hydrophobic Sn-Beta catalysts than their hydrophilic analogues. These differences in reactivity result from entropic penalties invoked upon reorganization of solvent molecules within hydrophilic reaction pockets during glucose isomerization which are inconsequential in hydrophobic zeolites. In the second example, the inclusion of low concentrations of alkyl chloride promoters (2-7 ppmv) in the feed modulates observed reaction rates, reaction orders, and ethylene oxide selectivity, and requires inclusion of alkanes in the feed in order to moderate the chlorine coverage and avoid formation of bulk chlorides. I will describe these effects of chlorine on ethylene epoxidation kinetics as well as methods we have developed to quantify the chlorine coverage as a function of process conditions, allowing us to report trends in ethylene oxide formation rates and selectivities as a function of Cl coverage. These case studies demonstrate that consideration of secondary effects of the reaction environment, not previously included in descriptions of catalytic reactions, are critical to accurately describe surface catalyzed reactions.

Biographical Information:

James W. Harris received a bachelor's degree in Chemical Engineering from the University of Virginia in 2012. He received a PhD in Chemical Engineering from Purdue University in 2017. His doctoral studies on the synthesis, characterization, and catalysis of Lewis acid sites confined in siliceous matrices were performed under the co-advisement of Professors Fabio Ribeiro and Rajamani Gounder. In September 2017, he began his present appointment as a postdoctoral scholar in the Department of Chemical

Engineering and Materials Science at the University of Minnesota under the supervision of Professor Aditya Bhan, where his work focuses on determining the role of promoters on ethylene epoxidation catalysis.