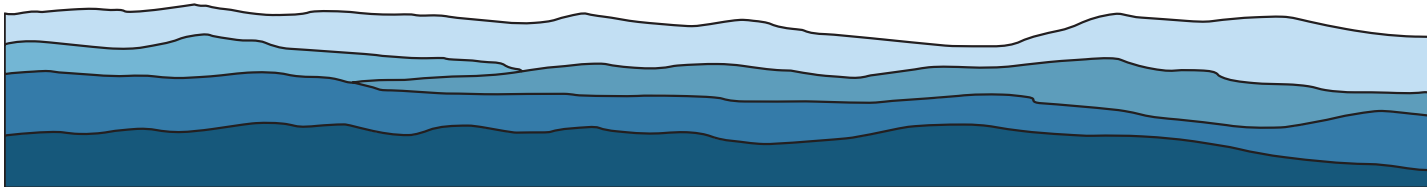


HIGHLANDS IN CHEMISTRY SEMINAR SERIES



YURIY ROMAN

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

"Leveraging solvent structure and electrostatics to accelerate reaction rates at heterogeneous catalytic interfaces"

FEBRUARY 9, 2024

2:30PM ET

HAHN HALL NORTH 140

FACULTY HOST:
GREG LIU

Heterogeneous catalytic reactions performed in condensed media inevitably occur at solid-liquid interfaces where complex interactions among interfacial solvent molecules, solid surfaces, and adsorbed intermediates modify reaction free energy landscapes. Biological catalysts navigate such complex free energy landscapes by manipulating solvent molecules to facilitate catalytic transformations via specific arrangements of hydrophobic and hydrophilic residues. These precise architectures regulate the structure of occluded solvent and substrate molecules along the reaction coordinate to grant enthalpy-entropy compromises which alter reaction free energy landscapes and enhance observed turnover rates. In addition, in biological catalysis, amino acid residues within enzyme active sites are known to sustain enormous electric fields that can drive catalysis. For example, in the case of ketosteroid isomerase (KSI), an enzyme important in steroid biosynthesis and degradation, steroid tautomerization rates are accelerated 105-fold by the electric field present in the active site. In this presentation, I will discuss recent efforts in our group to use such "unconventional" handles to manipulate the reactivity of heterogeneous catalysis.

In the first part, I will show our recent work on how to harness spontaneous electric fields to direct thermochemical catalysis. While it is known that intrinsic electric fields play an important role in molecular and biological catalysis, their role in heterogeneous thermochemical systems remains unclear because the catalysts employed are typically disconnected from an external circuit (thus making it difficult to monitor or control the degree of electrical polarization of the surface). We addressed this knowledge gap by developing general methods for wirelessly monitoring and controlling spontaneous electrical polarization at conductive catalysts dispersed in liquid media. Our work showed that rates for non-polar reactions are significantly influenced by spontaneous electric fields and demonstrated that interfacial electric fields should be considered alongside temperature, reactant activities, and catalyst structure as critical parameters to understand liquid-phase heterogeneous catalysis.

In the second part, I will show how we demonstrated that, akin to the way enzymes increase reaction rates by organizing solvent structures, pore polarity in zeolites can be exploited to order solvent networks to stabilize transition states and achieve a 10-fold increase in hydrogen transfer rates. Specifically, the more tightly ordered 2-butanol H-bonding network present in the pores of hydrophobic Beta zeolites stabilizes the transfer hydrogenation transition state to a greater extent than the liquid-like 2-butanol structure present in hydrophilic Beta zeolites, giving rise to enhanced turnover rates on the hydrophobic catalyst. Furthermore, reactant adsorption within hydrophobic Beta zeolites is entropically-driven by the breakup of intraporous H-bonding solvent-solvent interactions that result in a net increase in solvent disorder. Indeed, the disruption of ordered water molecules confined within hydrophobic reaction pockets alters the energetics of adsorption and catalysis, but a mechanistic understanding of how nonaqueous solvents influence catalysis in microporous voids has remained unclear. Our work shows how the ability of the zeolite pore to control the structure of confined nonaqueous solvents offers a unique dimension for the design and engineering of microporous adsorbents and catalysts beyond the active site.

Prof. Yuriy Román obtained his Bachelor of Science degree in Chemical Engineering at the University of Pennsylvania in 2002 and completed his Ph.D. at the University of Wisconsin-Madison, also in Chemical Engineering, under the guidance of Prof. James Dumesic in 2008. Next, he completed a two-year postdoc at Caltech, working with Prof. Mark E. Davis on the synthesis of zeolites. Prof. Román joined the department of Chemical Engineering at MIT as an Assistant Professor in 2010, where he was promoted to Associate Professor in 2014 and Full Professor in 2020. The core of his research lies at the interface of heterogeneous catalysis and materials science, where he combines catalyst design, kinetic studies, and reaction engineering study the chemical transformation of molecules within reactive microenvironments. His research portfolio includes projects in biorefining, hydrocarbon conversion, porous materials, and electrocatalysis. In addition to receiving an NSF Career Award in 2014, he also received two inaugural young investigator awards: the ACS Early Career in Catalysis Award and the AIChE Catalysis and Reaction Engineering Division Young Investigator Award. In 2018, he also received the Rutherford Aris Award granted by NASCRE and the Robert Augustine Award by ORCS. In 2022, he was selected as a finalist for the National Blavatnik Award in Chemistry, and in 2023 he received the Paul H. Emmett Award in Fundamental Catalysis.