

CHEMICAL, BIOLOGICAL & MATERIALS ENGINEERING

100 E. Boyd, Sarkeys Energy Center, T-301

405-325-5811

The University of Oklahoma

Norman, Oklahoma

2014 – 2015 Seminar Series

DR. ROBERT RIOUX

FRIEDRICH G. HELFFERICH ASSOCIATE PROFESSOR OF CHEMICAL ENGINEERING
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA

Will present a seminar on

“INTERROGATING BURIED SOLID-LIQUID CATALYTIC INTERFACES WITH CALORIMETRY: EXAMPLES FROM BIOMASS CONVERSION AND CATALYST SYNTHESIS”

Ligand-receptor interactions in biological systems are quite diverse, as exemplified by the range of energy that they span; weak binding systems display dissociation constants (K_d) with millimolar affinity, while tight binding systems can have affinities as high as pico- to femtomolar. Interactions between ligands, substrate, and solvent within organometallic and heterogeneous catalytic cycles are of the same magnitude with respect to their pairwise interactions. For decades, biochemists and biophysicists have utilized isothermal titration calorimetry (ITC) to measure the thermodynamic binding profile of numerous ligand-receptor combinations. ITC or other types of solution calorimetry have found limited applications in inorganic or materials chemistry. We demonstrated recently the extension of ITC to the study of solvated organometallic, nanoparticle and heterogeneous catalytic systems.

This presentation will focus on two areas where solution-phase calorimetry can provide critical insight that can't be recovered by any other technique. In the area of biomass conversion, we demonstrate solution-phase calorimetry can be used to quantitatively determine the impact of inner- or outer-sphere modification of homogeneous and heterogeneous acid catalysts on the ability of these catalysts to tolerate water inhibition. We utilize the esterification of small organic acids in organic solvents with added water as a model reaction. We demonstrate “inner-sphere” modification of the R group of homogeneous sulfonic acids ($ROSO_2H$) influences not only the acidity of the sulfonic acid group but also the heat of solvation of the sulfonic acid in water/1,4-dioxane mixtures. The influence of the hydrophobic backbone is quickly negated as the water content increases demonstrating increased separation between the proton and conjugate base. “Outer-sphere” modification of sulfonic acid grafted silica can lead to additional tolerance to water inhibition. We demonstrate heats of wetting of modified sulfonic acid modified silica can be decreased considerably. The kinetic consequence of the reduced heat of wetting is a corresponding decrease in the inhibition of water on the rate of the esterification reaction.

The method of catalyst synthesis has been known for decades to determine the final physicochemical properties of the catalyst but there has been little discussion in the literature of the influence that solution-phase processes have on the final catalyst properties (i.e., particle size, distribution, composition). Catalyst synthesis is initiated at a solid-liquid interface and quantification of the thermodynamics of transition metal precursor binding to the solvated amphoteric metal oxide or carbon surface has only been measured recently. We will demonstrate the magnitude of this interaction – using examples of both electrostatic and covalent – is critical to understanding the stability of noble metal-based heterogeneous catalysts during pretreatment (calcination/reduction). Utilizing synchrotron-based high energy x-ray scattering with pair distribution function (PDF) analysis, we demonstrate the magnitude of this initial interaction correlates with the overall particle size and distribution after pretreatment.

THURSDAY, SEPTEMBER 25, 2014
COOKIES AND COFFEE -- 1:45 P.M.
SEMINAR -- 2:00 P.M.
SARKEYS ENERGY CENTER, ROOM M-204

THIS IS A REQUIRED SEMINAR FOR CHE 5971

Accommodations on the basis of disability are available by contacting the office.