

Louise Berben, UC Davis

Metal cluster electrocatalysts: fast proton transfer and selective formate formation from CO₂

Plenary talk abstract

In this talk I will discuss metal carbonyl clusters that have delocalized bonding and electronic structures that can serve as models for the regime of nanoparticle (electro)catalysts. The intermediate size of these clusters, between molecules and nanoparticles, preserves access to the powerful characterization tools of molecular chemistry to enable a thorough characterization of structures and reactivity using tools such as single crystal X-ray diffraction and cyclic voltammetry (CV). The kinetics of heterogeneous electron transfer, diffusion properties, and reactivity with protons and CO₂ will be presented to benchmark physical and reactivity properties of cobalt and iron clusters including [Co₁₃C₂(CO)₂₄]⁴⁻, [Co₁₁C₂(CO)₂₃]²⁻, and [Fe₄N(CO)₁₂]⁻. For large Co clusters, protonation of the cluster following reduction occurs at a rate of 10⁹ s⁻¹, and a reaction mechanism for H₂ evolution from protons will be discussed. The different clusters have mechanistic features in common with each other, and these are distinct from the mechanisms of molecular electrocatalysts: for example, following fast formation of the cluster-hydride intermediate, the rate for hydride transfer to a substrate, such as proton or CO₂, is gated by the hydride donor ability of the cluster-hydride (and this is correlated with the redox potential of the cluster). Protonation and hydride migration events on all of the cluster cores are coupled with electron transfer events in these reactions. I will also illustrate the potential for product selectivity that arises from these distinct PT properties; selective hydride transfer to CO₂ for formate formation is one example.