Charge Transfer Reactions at Metal–Organic Framework-Liquid Interfaces

Charge transfer reactions at solid-liquid interfaces play a critical role in reactions relevant to the energy and chemical sectors. In a protic medium, these charge transfer reactions almost always involve proton-coupled electron transfer (PCET) reactions with equimolar amounts of protons and electrons; this is thermochemically equivalent to an H-atom transfer reaction. The thermodynamics of H-atom binding to the electrocatalyst surface has long been considered the 'catalytic descriptor' that scales with the overall activity of these reactions, resulting in a volcano-shaped plot (the Sabatier Principle). Typically, these binding energies are computed on defect-free crystalline surfaces, which minimally represent the complex surface structure of the experimentally employed catalysts; these catalytic motifs can dynamically evolve in their structures during the reaction. The lack of structural understanding of surface catalytic sites during electrocatalysis further precludes atomically precise knowledge of the reaction thermodynamics, kinetics, mechanism, and many other critical factors in deriving catalyst design principles.

We describe our recent efforts in employing redox-active, Ti- and Ce-based metal–organic frameworks (MOFs) as model electrochemical systems to elucidate the thermodynamics and kinetics of PCET reactions with atomic-level structural precision. Through electrochemical and computational approaches, we established the H-atom binding energy at metal-oxo nodes of these MOFs, which we refer to as MO–H bond dissociation free energy (BDFE; M = Ti^{3+} or Ce^{3+}). BDFEs were largely independent of the chemical composition of electrolytes, suggesting that these values are intrinsic to the MOFs. In contrast, PCET kinetics within the extended lattice structure are highly sensitive to the electrolyte composition, challenging implicit assumptions within the catalysis field and beyond. We will conclude with our more recent efforts in examining redox reactions beyond PCET, including sodium-coupled electron transfer reactions. Implications of these results regarding energy-relevant catalysis will be discussed.