

## Control of Catalysis at Interfaces by Applied non-Faradaic Electric Fields

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Non-Faradaic electric fields can be used to tune molecular properties and control catalytic reactions at interfaces, although a molecular-level understanding of the underlying control mechanisms have been hindered by the complexity of interfacial environments. The Yale-Emory-UCSD team funded by the AFOSR, has combined its diverse expertise in theory, spectroscopy and synthesis/electrochemistry to study interfacial electric fields to exploit them in electrocatalytic applications. We have computationally demonstrated that electric fields can precisely modulate the hydricity of iridium (III) half-sandwich complexes adsorbed on gold electrodes. The range of accessible hydricities exceeds that which has been accessed through chemical substitution, without the need for any synthetic changes to the molecule. The vibrational Stark effect allows for the electric field at the catalytic center to be measured experimentally, and correlates with the hydricity of the catalyst. In recent work, we have developed a Stark-shift molecular ruler for mapping interfacial electric field profile through the Helmholtz double layer in contact with an electrode surface. We synthesized molecular adsorbates with localized vibrational probes tailored with suitable anchoring groups and various lengths for probing the interfacial electric field when immobilized on the electrode surface. Preliminary results on tungsten-carbonyl-isocyanides probes show well-defined spectroscopic signatures that monitor the Stark shift as influenced by the interfacial field as characterized by field dependent vibrational spectroscopy and computational modeling. Furthermore, we have analyzed the interplay of non-Faradaic and Faradaic electric fields on CO<sub>2</sub> conversion to CO on Cu surfaces, highlighting the power of combined sum frequency generation spectroscopy with computational modeling to elucidate the nature reaction intermediates as a function of applied bias potentials. Bending frequency, potential shift, and isotopic shift experiments provide robust characterization of the mechanism based and clarity on competitive binding of intermediates as influenced by applied potentials on metal surfaces. Looking more deeply at how the defects on metal surfaces modulate interfacial electric fields and impact catalytic processes, we have explored defects on Au(111) surfaces and their influence on CO<sub>2</sub>/CO conversion. Examining adsorption motif, coordination numbers and CO vibrational frequency shifts, we have identified the characteristics of specific defects that find a balance between CO<sub>2</sub> adsorption and CO desorption while maintaining an energetically favored reaction. We find experimental probes that could be used for detected defects with optimal functionality. In collaboration with Pfefferle (Yale), we have also explored hematite surface defects on CH<sub>4</sub> oxidation, revealing the evolution of reaction intermediates formed via a tetra-iron center with an antiferromagnetically coupled iron dimer reaction site.