

## Enabling Predictive Science for Catalysis under Uncertainty

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Structure sensitive reactions, such as the oxygen reduction reaction (ORR), are important in renewable energy transportation and storage technologies, such as fuel cells. For these reactions, catalyst surface structure can alter the rate by several orders of magnitude and can change during reaction. Despite the importance of surface structure, the ability to model structure sensitive reactions with quantitative precision is lacking for two reasons. First, structure sensitive rates for complex surfaces cannot be computed efficiently as the active site is usually unknown. Second, models built with simple surfaces are often incompatible with the complex materials used for commercially relevant chemical processes. This latter problem requires characterization of structure from experimental data and is known, in catalysis, as the materials gap. Quantitatively accurate kinetic models and operando characterization methodologies constitute two missing pillars of predictive catalyst science.

To tackle efficient kinetic modeling for structure sensitive reactions, we develop a site-specific mean-field microkinetic model for the ORR. To our knowledge, this is the first model that couples long-range solvation and coverage interactions with short-range interactions of the active site. We capture short-range interactions by scaling binding energies with the generalized coordination number (GCN) of the active sites. We find that the impact of these short-range interactions on reaction rates is influenced by the morphology of the active site. For structure optimization, scaling binding energy with GCN has proven successful. If the type of material is included as a design variable, additional methods are needed.

In addition to electronic energy, entropy and heat capacity influence reaction rates. These temperature effects depend upon vibrations for adsorbed systems. To incorporate these effects for improved catalyst design, we develop theory to predict the scaling of adsorbate vibrations across transition metal surfaces and between active sites, including transition states. We demonstrate that vibrational scaling can impact coverages by almost 50% for the competitive adsorption of carbon monoxide (CO) and molecular oxygen. Beyond improving kinetic models, we show that these scaling relations can be used in identification of reaction intermediates.

Kinetic models require knowledge of the physical catalyst surface and how this surface changes during reaction. To this end, we develop a characterization framework to obtain distributions of active sites given probe molecule spectra. This methodology includes generating hundreds of thousands of complex synthetic spectra from simple spectra of CO on platinum (Pt) nanoparticles. We train neural network models on these spectra to map spectra to structure and develop theory to identify the suitability of spectroscopic probe molecules for discriminating structural descriptors. Ultimately, we find that ethylene is ideally suited for identifying the GCN of Pt active sites.

Throughout this thesis we develop computational methods that enable predictive catalysis. We do this by combining physics- and data-based methods with uncertainty quantification for kinetic modeling and computationally-aided characterization in a modular fashion. Thus, as more accurate data is made available, it can be inserted into an already developed framework. By incorporating data into portions of the models that would either be inaccurate or too computationally intensive to model directly, we facilitate model predictability.