

Fine-tuning the microenvironment of the active site on a heterogeneous catalyst for selective chemical transformation

Abstract

For billions of years, nature has evolved enzymes that can catalyze reactions efficiently to help all the life on earth survive. Today, to meet the global demand of the human population, we need enzyme-like selectivity and efficiency in highly scalable heterogeneous catalysis. This need is particularly critical for challenging transformations, such as converting biomass-derived sugars into fuels and high-value chemicals, addressing pressing sustainability challenges. This thesis envisions a futuristic biorefinery capable of selectively producing desired high-value chemicals with high yield. While simple kinetic or thermodynamic correlations derived from volcano plots have helped accelerate catalyst selection, they have limited the ability to fine-tune product formation rates and yields. To achieve high efficiency in such operations, catalyst designs have developed beyond one-dimensional descriptor-based protocols toward three-dimensional microenvironment perturbations at the active site.

With the help of molecular simulations, this thesis delves into four strategies to fine-tune the local environment around the active site, which are continuously enhancing the performance of heterogeneous catalysts to address the challenges of a futuristic biorefinery. These strategies are: (a) developing multiple active centers, each with a unique role in selective transformations; (b) stabilizing substrates/reactants via a hydrogen-bond network to facilitate proton transfer; (c) enhancing proton-coupled electron transfer (PCET) mechanisms driven by electric field and pH alterations at the electrode–electrolyte interface; and (d) increasing the stability of the active site through confinement.

Chapter 1 discusses a review of these strategies that help fine-tune the catalytic reactivity, selectivity and stability crucial in the biorefinery viewpoint. **Chapter 2** presents all the computational methods used in this thesis to study the potential energy surface for kinetic and thermodynamic analysis using *ab initio* density functional theory, molecular dynamic simulations and machine learning potentials. **Chapter 3** describes the breaking of descriptor-based linear scaling relations on Cu-based single atom alloys showcasing the advantages of multiple active centers. In **Chapter 4**, the stability analysis of dispersed transition metal nanocluster with confinement effect in zeolite is discussed in detail. The structure sensitivity

of CO₂ electrochemical hydrogenation reaction on Cu-based alloys is exhibited in **Chapter 5** with the role of solvents, ions, and coverage. **Chapter 6** highlights the role of electric potential, pH and solvents on Cu catalysts for benzaldehyde hydrogenation. Finally, in summary and outlook (**Chapter 7**), the thesis describes the efforts to undertake rational catalyst design that can yield precise selectivity with each active site playing a unique role using simulations.

This dissertation highlights the interplay of geometric, electronic and confinement effects at the active site. The complexity of an active site is just not restricted to which surface, facet, or zeolite it is part to—but also involves the effect due to electronic interactions with adsorbate and the reaction conditions involving pH, solvents, ions and electric field. This makes designing new catalysts and identifying mechanistic routes fascinating in heterogeneous catalysis. The underlying theme of this dissertation is understanding these complex effects through mechanistic insights with model reactions for hydrocarbon valorization in a futuristic biorefinery.