

Mechanistic Insights and Catalyst Design for Carbon Neutrality

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With the drive toward carbon neutrality, converting carbon-rich wastes, such as biomass and waste plastics, into fuels and valuable chemicals has attracted a surge of interest, for addressing the energy transition and environmental concerns. To improve the conversion efficiency and circumvent harsh reaction conditions, innovations in heterogeneous catalysts and catalytic systems are imperative. However, achieving this goal is daunting due to the multidimensional complexity of heterogeneous catalysis in terms of active site uncertainty and reaction pathway diversity, especially for biomass and plastics systems in which reactants are complicated. This thesis addresses these challenges by computational modeling in collaboration with experimental work, revealing the importance of microenvironment, impurity, structure flexibility, and defects in determining the nature of active sites and reaction mechanisms.

First, we construct a framework incorporating data science, density functional theory (DFT) calculations, experimental synthesis, and characterization to clarify the active sites in carbon-based catalysts. Chapter 2 investigates the Brønsted acidic oxygen-containing functional groups for dehydration reactions, which are important for biomass upgrading. We demonstrate the stronger acidity of the phenolic group than that of the carboxylic group because of the special carbon environment, making it the dominant active site. Chapter 3 focuses on the N-doped carbon catalysts for hydrodeoxygenation (HDO) of 5-hydroxymethylfurfural (HMF). We elucidate that traces of Fe impurity, instead of abundant nitrogen species, contribute remarkably to the catalytic performance. DFT calculations show that the Fe single site, i.e., the Fe-N₃ site, can promote HMF adsorption and H₂ activation, which may be the true active site.

Second, inspired by the importance of the Fe single atom in Chapter 3, we pay attention to developing high-performance Fe-N-C catalysts for catalytic transfer hydrogenation (CTH) of furfural through understanding the key factor affecting reaction pathways and exploring structure-activity relationships. In Chapter 4, we fabricate a highly active Fe-N-C catalyst with a turnover frequency of 1882 h⁻¹. We use XANES simulations, DFT calculations, and microkinetic modeling (MKM) to determine a defective, flexible Fe-N₃ site as the dominant active site and reveal the critical role of site flexibility in tuning reaction pathways and thus improving activity. Chapter 5 utilizes the concept of site flexibility to figure out the activity descriptor for the CTH of furfural. By defect engineering, we regulate the Fe-N bond lengths, i.e., the Fe-N₃ site's flexibility, and unravel its profound impact on the CTH activity. Molecular orbital interaction analysis provides physical insights into this observation. We eventually build the structure-activity of Fe-N₃ sites with the Fe-N bond length as a geometric descriptor.

Lastly, in addition to the catalyst activity, we extend our focus to the impact of impurity in reactants on stability. In Chapter 6, we develop an efficient workflow containing structural similarity, DFT calculation, group additivity (GA) model, and Redhead analysis for predicting the heats of adsorption and, thereby, desorption temperatures of a broad range of plastics additives in Brønsted acidic zeolites. This guides optimizing reaction temperature to remove additives thermally, which is essential to mitigate the deactivation effect of additives on the Brønsted acid sites.

In summary, this thesis shows the critical role of computational modeling in clarifying active sites, investigating reaction mechanisms, establishing structure-activity relationships, and improving catalyst stability, which is imperative to reach a sustainable future.