Abstract

Heterogeneous catalysis in petroleum refining and gas processing, such as fluid catalytic cracking (FCC) and steam methane reforming (SMR), has developed as a high-temperature, gas-phase technology designed for hydrocarbon or gaseous feedstocks. The emergence of biomass valorization and electrochemical energy technologies has fundamentally altered this perspective. Oxygen-rich biomass-derived molecules are inherently soluble in water, requiring catalytic reactions to proceed in aqueous environments. In these systems, water strongly influences catalytic reactivity through its polarity, hydrogen-bonding capability, and ability to stabilize charged intermediates and transition states. Hydrogen-bond networks formed by water molecules can mediate proton transfer, reorganize local solvation structures, and reshape reaction free-energy landscapes. At the same time, water can introduce competing interactions, including strong solvation of reactants or intermediates, competitive adsorption at catalytic active sites, and energy-intensive product separation challenges. In electrochemical reactions such as the oxygen evolution reaction (OER), water also participates directly as a reactant, where its activation and subsequent proton-coupled electron transfer steps determine catalytic efficiency. These diverse interactions highlight the need for a molecular-level understanding of how water influences catalytic mechanisms across different catalytic environments.

This thesis investigates the influence of water across homogeneous, confined heterogeneous, and electrochemical catalytic systems using density functional theory (DFT)**,** ab initio molecular dynamics (AIMD)**,** and advanced free-energy sampling techniques including well-tempered metadynamics and the string method in collective variables**.** These computational approaches enable explicit characterization of solvent structures, hydrogen-bonding networks, and solvent-dependent reaction pathways.

Chapter 3 examines Brønsted acid–catalyzed dehydration of mevalonolactone (MVL) in bulk solvents including water, tetrahydrofuran (THF), and THF–water mixtures. A mechanistic descriptor based on the coordination number of solvent molecules interacting with the cyclic ester functionality captures solvent-dependent mechanistic shifts and correlates with both experimental conversion trends and calculated activation barriers. The results demonstrate that replacing water with THF alters local hydrogen-bonding environments and proton transfer pathways, lowering the dehydration free-energy barrier.

Chapter 4 explores solvent effects within the confined microporous environment of HBEA zeolite, where confinement generates structured hydrogen-bond networks that facilitate proton shuttling and reorganize the reaction free-energy landscape. Changing the intrapore solvent from water to aprotic media such as THF modifies adsorption strength, transition-state stabilization, and the identity of the rate-limiting step. Chapter 5 further investigates solvent-controlled mechanisms through acetone self-aldol condensation in HBEA zeolite. Solvent polarity governs competitive adsorption and stabilization of intermediates, shifting the rate-determining step from keto–enol tautomerization in aqueous environments to carbon–carbon coupling in hydrophobic solvents such as decalin.

Chapter 6 focuses on the oxygen evolution reaction on Mn-doped Co_3O_4 catalysts under acidic and saline conditions. Explicit solvation models reveal stabilization of key surface intermediates (OH*, O*, and OOH*), while manganese incorporation enhances catalyst stability and suppresses chlorine adsorption, improving selectivity against the competing chlorine evolution reaction in saline electrolytes.

Together, these studies provide a unified molecular-level understanding of how water influences catalytic reactions through solvation, hydrogen-bond-mediated proton transfer, and direct participation in the reaction such as in OER. By elucidating these roles across different catalytic environments, this dissertation provides insight into how solvent structure, confinement, and catalyst composition can be leveraged to design improved catalytic materials and reaction environments for biomass conversion and sustainable energy technologies.