

A Multiscale Sampling Model for Calculating Energies, Free Energies, Activation Energies, and Rate Constants of Heterogeneously Catalyzed Reactions under Liquid Phase

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Density Functional Theory (DFT) is necessary for calculating the energies of catalytic reactions, but accurately and efficiently modeling catalysts in the liquid phase remains a challenge because of complexity at the liquid/solid interface. This complexity arises from a variety of phenomena, deriving from interactions between solvent molecules and adsorbates on the catalyst surface. These interactions give rise to dispersion forces, hydrogen bonding, and chemical bonding between solvent molecules and surface species, which influence the energies and the entropies of the reaction intermediates and additionally provide alternate kinetic pathways for certain elementary steps. Since the liquid molecules are configurationally disordered, meaning that there are many possible ways the liquid molecules can arrange spatially around the catalytic species, modeling catalysis in liquid phase depends on being able to capture the various configurations of liquid molecules and as well as their various influences on catalytic thermodynamics, kinetics, and mechanisms. Capturing this configurational disorder cannot be accomplished with quantum mechanics-based methods, as quantum mechanics is too computationally expensive to explore multiple distinct configurations of liquid molecules. In this work, we aim to capture molecular level catalytic phenomena under liquid conditions by combining DFT and classical molecular dynamics (cMD). Specifically, we use cMD to generate configurations of liquid molecules and DFT to observe and calculate the energetics of bond breaking and forming processes that result from these configurations. We demonstrate this “multi-timescale” model for calculating energies, free energies, activation energies, and rate constants of catalytic reactions in liquid conditions. We further show how it can be used as a starting point for *ab initio* molecular dynamics simulations, which can be used to observe bond breaking and forming and conformational effects.