

4w Density Functional Theory Studies of Acid Catalysis and Electrocatalysis

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My research employs density functional theory quantum-chemical methods to study problems of interest in heterogeneous catalysis and materials research, more generally. These methods are used to calculate reaction energies and activation barriers, which are then input into kinetic models that include realistic reaction conditions (temperature, pressure) to provide molecular level insight into the factors that control catalyst activity and selectivity. Specifically, my doctoral research seeks to understand the role of water in the deactivation and regeneration of polyoxometalates for acid catalysis. As a post-doctoral researcher, I am currently studying the molecular pathways of the catalytic reactions within the direct methanol fuel cell. A realistic model of the electrocatalytic system, in which both the solution phase and an applied potential are included, is employed to aid in the design of effective materials for methanol oxidation and oxygen reduction. Polyoxometalates, or heteropolyacids (HPAs), have been shown to be active for reactions requiring a strong acid catalyst, such as the alkylation of isobutane with butenes, and are a potential replacement for the corrosive, toxic liquid acids currently used. However, deactivation with time on stream has prevented their industrial application. Density functional theory (DFT) is used to investigate the energetics of proposed deactivation mechanisms. Reaction energies and activation barriers are determined by DFT and further used to establish reaction rates and equilibrium constants to clarify whether a proposed mechanism may explain the deactivation process. Emphasis is placed on understanding how including water in the reaction environment may slow or prevent deactivation. This research also seeks to further our understanding of acid-catalysis mechanisms over heteropolyacids by providing insight into the requirements of an effective solid-acid catalyst for the alkylation of isobutane and n-butene. Heteropolyacids may also be applied as additives to proton conducting membranes. Over the surface of HPAs, the activation barrier for proton transport as H_3O^+ is an order of magnitude lower than that for anhydrous proton conduction. The use of ab initio methods to calculate the rate constant for proton transport and the equilibrium constant for water adsorption allow prediction of the rate of proton transport as a function of temperature and water partial pressure. The inclusion of water greatly increases the rate of proton transport, however at higher temperatures the desorption of water leads to a decrease in proton conductivity.