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Title: Density Functional Theory Investigations of Zeolite and Intermetallic Alloy Active Site Structures for Kinetics of Heterogeneous Catalysis
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Catalysis has a responsibility to provide solutions to the growing grand challenge of sustainability in the fuels and chemical industry to help combat climate change. These changes; however, cannot be realized without a more fundamental understanding of the active sites that catalyze chemical reactions, and how they can be tuned to control rates and selectivities. Four specific examples of active site modification will be considered in this work: the speciation of isolated metals in zeolite frameworks, solvent thermodynamics and structure at defects in zeolite frameworks, the electronic modification of platinum through alloying in well-defined intermetallic nanoparticles, and the mobility and shape of gold nanoparticles in zeolite channels. Each will highlight how quantum chemistry calculations provide a fundamental understanding of how these active site modifications influence the kinetics of chemical reactions, and how they can be controlled to pursue solutions to the short-term reduction of carbon through sustainable utilization of shale gas as well as long term renewable chemicals production through biomass upgrading.

Zeolites exchanged with metal heteroatoms can behave as solid Lewis or Brønsted acids depending on heteroatom identity. Lewis acid heteroatoms can adsorb water and hydrolyze to speciate into “open sites” which have been shown to differ in their ability to catalyze reactions such as glucose isomerization as compared to “closed sites” which are fully coordinated to the zeolite framework. The structure and catalytic properties of these sites are interrogated by a gas phase reaction, ethanol dehydration, in Sn-Beta by a combined Density Functional Theory (DFT) and experimental study. DFT is used to map the possible reaction mechanisms for ethanol dehydration, including the speciation of Sn sites into hydrolyzed configurations from water or ethanol. Power anharmonic entropy methods using *ab-initio* molecular dynamics (AIMD) is used to capture the entropy of confined reactive intermediates, which is shown to be necessary to compare with experiment. A microkinetic model for ethanol dehydration including unselective and inhibitory intermediates is constructed. This microkinetic model predicts the population of reactants and products on the catalyst surface as well as the sensitivity of individual elementary steps to the total rates. Results on closed and hydrolyzed open zeolite sites can then be compared with ethanol dehydration on

“defect open” sites which were shown experimentally to occur at grain boundaries. A grain boundary model is constructed of zeolite Beta, where unique sites have similar ligand identity as hydrolyzed open sites. These defect open sites are found to not contribute to the observed reaction rate as they cannot stabilize the same transition state structures that were observed in internal Beta sites.

Intuition about the ethanol dehydration reaction in Sn-Beta was then used to map a more expansive and diverse chemical network, the synthesis of butadiene from acetaldehyde and ethanol. For elementary reactions in this mechanism, which included aldol condensation, MPV reduction, and crotyl alcohol dehydration in addition to ethanol dehydration, the hydrolyzed open sites were found to be crucial reactive intermediates. Hydrolyzed sites were necessary to stabilize favorable transition states, which requires reconstruction of the local framework environment. Methods to preferentially stabilize hydrolyzed sites were then explored, using a screening algorithm developed to consider all possible sites in each zeolite framework. It was found that the stability of these hydrolyzed sites could be correlated to the local strain exerted by the surrounding silica matrix. This provides a new descriptor that stabilizes intermediates relevant to the synthesis of butadiene and ethanol dehydration.

Next, the structure and thermodynamic stability of water networks around Sn-Beta defects and heteroatom active sites was considered using AIMD. As many biomass reactions occur in the presence of water, the interactions of water with hydrophobic and hydrophilic functionalized defects dictate how reactive intermediates and transition states change in a solvating environment. Locally stable and strongly nucleated clusters of water were observed to form at Sn defects, with less densely packed water structures stable at hydrophilic defects. This is in comparison to defect-free siliceous Beta where significantly less water uptake is observed. These local clusters are in equilibrium with the less dense liquid-like phase that extends between defects. These results motivate localized cluster models around active sites in Lewis acids, as well as advance the fundamental understanding of hydrophobic/hydrophilic interactions in microporous materials. The local cluster models are then applied to the ethanol dehydration reaction in protonated aluminum Beta zeolites where experimentally observed non-unity coefficient ratios are rationalized by quantifying a different degree of solvation for the ethanol reactant state as opposed to the transition state, validated by a thermodynamic phase diagram.

Changes in the electronic energy levels of *d* electrons upon alloying was studied in conjunction with a new spectroscopic technique being performed at Argonne National Laboratory to develop new descriptors to predict the degree of coking for different alloys. Resonant Inelastic X-ray Scattering (RIXS) simultaneously probes the occupied and unoccupied valence states of platinum in nanoparticles at ambient conditions. The specific excitation process of this spectroscopy is particularly amendable to DFT modeling, which was used to provide richer chemical insight into how changes in observed RIXS signature related to the electronic structure changes of platinum upon alloying. From a suite of multiple 3d alloy promoter catalysts synthesized, a quantitative comparison with DFT modeled spectroscopy was developed. The stability of DFT calculated coke precursors, relevant to dehydrogenation catalysts to convert light alkanes into olefins, was then correlated to DFT modeled RIXS spectra, which is a better descriptor for adsorption of unsaturated chemical intermediates that used previously, as well as being a descriptor accessible to direct experimental usage.

Finally, the diffusion of gold nanoparticles in the TS-1 catalyst was studied using AIMD to help understand what structural motifs of gold are present under reaction conditions and how the shape and binding sites of gold is strongly influenced by deformation by the zeolite framework. This is used to help predict new zeolites for use in direct propylene epoxidation using molecular oxygen and hydrogen. The optimization of this catalyst is environmentally relevant to reduce the usage of inorganics and reduce the cost associated with production of hydrogen peroxide. Following these discussions, the role of computation in predicting the structure of active sites and kinetics in conjunction of experiment will be discussed. The broader impact of these findings will also be considered, which span beyond these specific reactions and materials.