ABSTRACT

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Title: First-Principles Studies of Transition Metal Catalysts for Electrochemical Reactions
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This thesis presents first-principles studies of electrochemical reactions at solid-liquid interfaces using transition metal electrodes within the framework of density functional theory (DFT). The thesis contains an extended introduction and three main sections of scientific results relating to nitric oxide (NO) electrochemical reduction on Pt and Cu surfaces, Brønsted−Evans−Polanyi (BEP) relationships for proton and electron transfer reactions on transition metal surfaces, and ethanol (CH_3CH_2OH) electrochemical oxidation on Pt. Each section contains a detailed discussion of the scientific motivation and results for the relevant application area. In addition, descriptions of tools that are adapted or developed to enable accurate and rapid modeling of the relevant electrocatalytic reaction networks are provided, including DFT calculations of electrochemical potential-dependent steps, kinetic Monte Carlo simulations of reaction networks, BEP's for general trends in reactivity, and strategies for estimation ofsolvation energies of adsorbed species.

The first section of this thesis focuses on the elucidation of pathways for NO electroreduction on Pt(111), Pt(100), Pt(211), and Cu(211) using a combination of first-principles calculations and electrokinetic rate theories. Different facets and types of surfaces are chosen as model electrodes to probe the structure sensitivity and understand how this affects on the activity and selectivity of NO electroreduction. Also, coverage- and potential-dependent reaction free energies and activation barriers for this reaction are determined. Barriers for chemical cleavage of N—O bonds on surfaces are found to be inaccessibly high at room temperature, implying that explicit electrochemical steps, along with the aqueous environment, play important roles in the experimentally observed formation of ammonia (NH_4^+) and nitrous oxide (N_2O). Use of explicit water models, and associated determination of potential-dependent activation barriers based on Butler-Volmer kinetics, demonstrate that ammonia is produced through a series of water-assisted protonation and bond dissociation steps on all surfaces. The first principles analysis from Pt(111) additionally shows formation of N_2O at higher potentials through an Eley-Rideal-type mechanism. On Pt(100), a combination of DFT and kinetic Monte Carlo (kMC) methods reveals that production of NH_4^+ can be traced to the rapid kinetics of N—O bond breaking in reactive intermediates, while rapid hydrogenation of surface N* species prevent competing pathways from forming either N_2 or N_2O. On the (211) step surfaces of Pt and Cu, the results suggest that product selectivity for NO reduction is different on Pt(211) and Cu(211). Pt(211) favors the formation of NH_4^+, while Cu(211) favors the formation of N_2O through *cis*-type (NO—NO)* dimers at saturated (0.5 ML) and NH_4^+ at low (< 0.17 ML) coverages. The catalytic pathways of Pt and Cu(211) are compared to corresponding pathways on the (111) surfaces. Taken in aggregate, the mechanistic studies provide a useful tool to describe the mechanism and energetics of metal-catalyzed electroreduction in the nitrogen cycle, and this approach should also find application to related electrocatalytic processes in oxygen and carbon cycle chemistry that are of technological and environmental interest.

The second section of this thesis involves the study of BEP relationships for proton and electron transfer reactions on close-packed transition metal surfaces. Linear energy relations are systematically studied using electrochemical protonation of surface nitrogen (N*) and NO*. Reaction energies and activation barriers are calculated at constant surface voltage in finite-sized unit cells via extrapolation to the infinite unit cell limit. The DFT results show that linear BEP relations are obtained from both elementary steps with different slopes. The slope of the BEP relationships can be directly related to the structure of the transition state, marking the first time that comprehensive BEP relationships have been established for proton-coupled electron transfer systems.

The third and final section of this thesis focuses on the electrochemical oxidation of ethanol on Pt surfaces. The study analyzes on solvation energies of reaction intermediates using explicit liquid water models based on ab initio molecular dynamic simulations (AIMD). The solvation energies are found to be closely related to the functional groups present in the ethanol oxidation reaction intermediates, as well as sterics of the intermediates, and they provide important energetic corrections that must be understood to accurately model the chemistry of this complex molecule.