ABSTRACT

Author: Choksi, Tej S. PhD
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Committee Chair: Professor: Jeffrey P. Greeley

The recent impetus towards preemption of runaway climate change through decarbonization of the global economy requires innovative solutions to the way energy is utilized and stored. This necessitates an inevitable transition to synthesis of chemicals and fuels using less carbon intensive feedstocks like natural gas, combined with renewable energy sources such as biomass, solar and wind. Catalytic processes will play a critical role in enabling these transformative technologies. Rapid developments in first principles techniques such as density functional theory (DFT) have facilitated the computational screening of a large ensemble of catalysts for sustainable energy solutions. Extending these paradigms to structurally and mechanistically complex molecular architectures, however, has emerged as a critical challenge to the field. This dissertation addresses this knowledge gap by elucidating reactivity trends on reducible metal oxides and bifunctional metal/oxide interfaces.

Reducible oxides, such as molybdenum trioxide (MoO_3), have widespread applications as partial oxidation catalysts in the chemical industry. Their reducible nature often engenders a rich interplay of catalytic chemistry and structural transformations. Partial oxidation of methanol is employed as a probe reaction to rigorously evaluate this interplay on MoO_3 (010) using DFT in conjunction with microkinetic modeling. Reaction kinetics are elucidated using an extensive reaction network comprising vacancy formation and oxidation, monomolecular dehydrogenation of methanol on reduced and non-reduced surfaces, bimolecular reactions between dehydrogenated intermediates, and precursor steps for hydrogen intercalation on MoO_3 (010). We estimate the impact of the surface oxidation state on the interplay between these pathways by varying the external pressure of oxygen in the microkinetic model, which reveals a volcano like dependency for the reaction rate. This analysis is extended to understand reactivity trends on doped MoO_3. We present periodic trends in vacancy formation energy, a key descriptor for activity trends in reducible oxide catalysts, as a function of dopant size and valence. The dopant has an intriguing

impact on both the extent of charge delocalization at oxygen vacancies and their local geometry, lending further fundamental insight into the complex interplay between structures of oxygen point defects and spatial arrangement of charge density for this model system.

We investigate the influence of exchange – correlation (XC) functionals on adsorption characteristics and reaction kinetics of methanol oxidation on MoO_3 using a descriptor-based approach involving scaling relations between XC functionals. Adsorption energies of intermediates and transition states calculated using BEEF-vdW are linearly correlated with adsorption energies obtained through several GGA, GGA-vdW, GGA + U, and hybrid XC functionals. Intercepts of these linear scaling relations are termed as the degree of binding, δ, and introduced as a descriptor for XC functionals. This represents an average difference in adsorption strengths, between BEEF-vdW and a given functional. The microkinetic model is parametrized in terms of δ using the scaling formalism, revealing the impact of XC functionals on reaction kinetics and rate determining steps. This approach should in principle, be extendable to other catalytic systems and provides a framework to easily quantify uncertainties in first principles derived microkinetic predictions from XC functional errors.

In addition to their intrinsic catalytic properties, metal oxides primarily function as structural supports for transition metal nanoparticles. They assist in controlling nanoparticle size by enhancing sintering resistance, and create bifunctional catalytic sites at the metal/oxide interface. These interfacial active sites in some specific cases possess enhanced catalytic turnovers in comparison to their individual counterparts. Our understanding of bifunctional promotion at interfaces is emerging, yet not at the level required for facilitating large scale screening. Although catalyst design considerations like scaling relations (SRs) and Brønsted Evans Polanyi type correlations (BEPs) are extensively explored on transition metals, oxide, and zeolites, such trends for bifunctional supported metal catalysts currently remain elusive. SRs are theoretical constructs that linearly correlate energies of complex surface species to atomic descriptors, enabling the parametrization of reaction networks in terms of energies of these descriptors. Considering doped Au/MgO (100) as a model bifunctional catalyst, we report the existence of SRs and BEPs for species participating in WGS, methanol synthesis, CO, and NO oxidation and NO reduction. Doping MgO releases electrons or holes to the Au/MgO interface, which in turn tunes adsorption strengths. Our analysis shows that SR slopes are not constrained by the bond order conservation (BOC) rule, which characterizes scaling slopes across a broad class of catalysts including metals, oxides, and zeolites. Their physical origin, instead, stems from electrostatic interactions at the metal/oxide interface. This phenomenon can potentially render greater flexibility in engineering the next generation of supported metal catalysts.

The last part of this dissertation describes two collaborative efforts combining atomistic modeling with catalyst synthesis, characterization, and kinetics testing, to comprehend structural transitions of multi-functional catalysts under working conditions. During in situ vacuum annealing, three-dimensional Au-Fe_3O_4 dumbbell nanoparticles transform into Au thin films, as the surface reduction of interfacial iron oxide proceeds. We corroborate the experimentally observed “anomalous” strong metal support binding using DFT derived thermodynamic arguments. Finally, using a similar ab initio thermodynamic approach, we confirm experimentally determined segregation trends, and their catalytic consequences, for two different structural forms of PtCu binary alloy nanoparticles that are post synthetically modified in gaseous CO and H_2 environments. Building on the fundamental insights in mechanistic details and reactivity trends charted out in this dissertation, I will conclude by delineating future directions that will ultimately facilitate the engineering of reducible oxides and bifunctional metal/oxide interfaces.