ABSTRACT

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One of the most important advances in modern theoretical surface science and catalysis research has been the advent of *Ab-Initio* Density Functional Theory (DFT). Based on the electronic structure formulation of Pierre Hohenberg, Walter Kohn and Lu Jeu Sham, DFT has revolutionized theoretical research in heterogeneous catalysis, electrocatalysis, batteries, as well as homogeneous catalysis using first-principles electronic structure simulations. Combined with statistical mechanics, kinetic theory, and experimental inputs, DFT provides a powerful technique for investigating surface structure, reaction mechanisms, understanding underlying reactivity trends, and using them for rational and predictive design of materials for various catalytic chemistries, including those that can propel us towards a clean energy future – for example water gas shift (WGS), methanol synthesis, oxidation reactions, CO_2 electroreduction, among many others. Fueled by advances in supercomputing facilities, early and numerous current DFT studies have been primarily focused on idealized simulations aimed at obtaining qualitative insights into experimental observations. However, as the immense potential of DFT has been unfolding, the demand for closer representation of realistic catalytic situations have rapidly emerged, and with it, the recognition of the need to reduce the disparity between theoretical DFT structures and real catalytic environments. Bridging this 'materials gap' necessitates using more rigorous catalyst structures in DFT calculations that can capture realistic experimental geometries, while at the same time, are creatively simplified to be computationally tractable. This thesis is a compilation of several projects on metals and metal/oxide systems that have been undertaken using DFT, in collaboration with experimental colleagues, with the goal of addressing some of the challenges in heterogeneous catalysis, while decreasing the 'materials gap' between theory and experiments.

The first several chapters of this thesis focus on bifunctional, metal/oxide systems. These systems are quintessential in numerous heterogeneous catalysis applications and have been the

subject of extensive study. More interestingly, they sometimes exhibit synergistic enhancement in rates that is greater than the sum of the individual rates on the metal (on an inert support) or on the oxide in isolation. Such bifunctionality often stems from the modified properties at the nanoscale interface between the metal and the oxide and is an active field of research. In particular, while a large body of literature exists that investigates the activity of metals, the role of the support in bifunctional systems is often uncertain and is the subject of investigation of the first few chapters of this thesis. We chose to study WGS on Au as support effects are particularly prominent on this system. The second chapter examines WGS on Au/ZnO, where realistic catalytic environment at the interface is reproduced by analyzing the thermodynamics of surface hydroxylation of the oxide under reaction conditions, and its effect on WGS kinetics is quantified through a microkinetic analysis. This study highlights the importance of considering spectator species which can drastically influence the energetics and kinetics of a reaction at a metal/oxide interface. In addition, fundamental aspects of the effect of surface hydroxyls on the electronic structure at the interface is also discussed.

The third chapter of the thesis builds on this theme and analyzes the effect of systematic perturbation of electronic structure at the interface through substitutional doping of the oxide. Chapters 3 and 4 focus on Au/MgO, a system which has been previously studied in extensive detail in our group and benchmarked through experiments. The effects of a series of dopants of varying electronic valences have been analyzed on a number of properties at the interface – vacancy formation energies, adsorption energies of intermediates, scaling properties, activation energy barriers and WGS activity. Exciting new scaling relationships are identified at this interface, having properties different from that observed on extended surfaces, and are interpreted using an electrostatic model. In the subsequent chapter, we identified Bronsted-Evans-Polanyi relationships for the different steps in the WGS pathway for a series of dopants. Coupled with the scaling relations, these trends are then used in conjunction with a dual-site microkinetic model to perform a volcano analysis for interfacial rates. Our analysis thus builds, for the first time, a rational design paradigm for electronic structure perturbation of the support at a bifunctional interface. The next chapter further investigates support effects, both geometric and electronic, in greater detail for Au supported on a series of oxide supports and discusses accelerated identification of an activity descriptor through a close fusion between computations and experiments.

In addition to interfacial effects of the support, this thesis also briefly examines a more apparent role of the oxide, wherein it influences the geometry of the supported metal. Two different Au-based systems are investigated using surface science approaches in Chapter 6 - the segregation properties of a bimetallic Au/Ir alloy on anatase and wetting behavior of Au-Fe_xO_y heterodimers – both of which are representative of the structural evolution of a supported catalyst under reaction conditions. Through our analysis, we show that the oxide directly influences these behaviors of the supported metal.

The next few chapters explore catalysis using metallic systems, focusing on transition metals, an important class of materials in heterogeneous catalysis and constitutes the major body of DFT literature for trends-based analyses. A crucial factor that contributed to the success of such high-throughput screening studies was identification of linear scaling relationships on transition metals, whereby the adsorption energy of complex molecular fragments was linearly related to that of simple atomic adsorbates. However, while these relationships are valid for low adsorbate coverages, at higher, catalytically relevant coverages, deviations from linearity are common, thus presenting a materials gap in volcano analyses. The incorporation of coverage effects, therefore, in scaling relations has been a pressing challenge. This thesis describes a simple means of systematically capturing changes in reaction energies due to coverage effects through a pairwise interaction model, where the changes in adsorption energies are shown to be a direct function of the number of neighbors and interaction parameters determined through DFT. In addition, we also draw a mathematical correspondence between scaling relations at high coverage and that at low coverage and discuss its implications on the existence of linear scaling relations.

The final few chapters discuss collaborative work on Pt based catalysts, an active catalyst for many chemical and electrochemical systems. We explore activity trends on bimetallic Pt based alloys and perform structural analyses on inverse oxides on Pt. These studies help understand the role of promoter in Pt based multicomponent catalysts