

Abstract

Catalysis will play a pivotal role in the transformation of the current chemical and fuel industries, driving efforts to mitigate greenhouse gas emissions, curbing the release of hazardous waste, and efficiently utilizing energy resources. Hence, it is crucial to establish a fundamental understanding of the active sites that drive chemical reactions and also the transformation of these active sites under varying reaction conditions. A particular class of catalysts which are extensively used in industrially relevant reactions, but not well understood, are metal nanoparticles supported over transition metal oxides. Under specific conditions the metal nanoparticles are believed to be partially covered by reduced, ultrathin oxide films, which can drastically transform the physical, chemical, and electronic properties of the catalyst surface. These transformations are often referred to as the Strong Metal Support Interactions (SMSI). The structure and chemical properties of the encapsulating SMSI overlayers can determine the reactivity, selectivity, and stability of the catalyst. To explore these phenomena, the encapsulating overlayers on metal nanoparticles are most effectively studied using ultrathin film models supported on single crystal transition metal substrates. In this thesis, periodic density functional theory (DFT) calculations, along with surface science experiments in collaborators' groups, are carried out to systematically study the molecular-level underpinnings of the metal oxide transformations.

As a starting point, we analyze the Pd/ZnO system. This is a potential methanol synthesis catalyst, and since ZnO is an irreducible oxide, it provides a test of the traditional hypothesis that partial reduction of support cations is necessary to exhibit SMSI. In order to compare our calculations with surface science experiments, where the ultrathin films are not in equilibrium with bulk species, we developed a mixed canonical – grand canonical phase diagram scheme. The scheme, when combined with exhaustive DFT calculations of many different ultrathin ZnO_xH_y film structures and stoichiometries, permits direct comparison of the calculated free energies of these disparate films. Although, the thin film models provide more well-defined conditions for studying SMSI, there are thermodynamic differences with the real SMSI system. These differences can be described by changing the thermodynamic ensemble used to analyze the DFT results and extrapolating to deduce the stability of films at realistic SMSI conditions. Using this formalism, we have discovered that ZnO_xH_y films on Pd, which don't exist in bulk, may form, and promote SMSI in irreducible oxides. This behavior is traced to both hydrogen incorporation in the films and strong stabilization of the films by the Pd substrates.

The computational framework, initially developed for the Pd/ZnO system, is subsequently extended to conduct thermodynamic investigations across different metal substrates. We found that linear scaling relationships (SRs) exist for the ultrathin films on metal surfaces that correlate the film formation energies with the combination of oxide cation and anion binding energies. However, these SRs deviate from classic bond order conservation principles. To provide an explanation for these deviations, and to enhance the predictive capabilities of the SRs, we introduced a generalized bonding model for oxy-hydroxy films supported on metal surfaces. By combining the SRs with grand canonical phase diagrams, we can precisely predict the stability of encapsulated films under specific reaction conditions. To validate the computational scheme, we apply it to the traditional SMSI system involving TiO_2 -supported metal nanoparticles. Our

calculations accurately predict which metals are prone to exhibit SMSI-like behavior and align well with available experimental results.

In order to analyze how these structures affect important real-world chemistries and identify key descriptors that influence their reactivity, we studied the adsorption behavior of common intermediates on oxide decorated metal surfaces. We first investigated two types of ultrathin films, the compact graphite-like ZnO and the open honeycomb-like $Zn_6O_5H_5$ on Pt(111). We found that the graphite-like ZnO islands barely affect the electronic properties of the Pt surface, while the honeycomb-like $Zn_6O_5H_5$ network tunes the surface electron density of Pt such that the binding site for CO shifts from on-top to bridge site. The findings enhance our understanding of metal-hydroxide interactions, potentially paving the way for innovative designs of highly efficient catalytic systems.

The SMSI effect is not confined to oxides used as supports. We confirmed the existence of a closely related phenomenon in Pt alloys, which are an important system for the oxygen reduction reaction (ORR). We identified elements which form stable oxy-hydroxy moieties on Pt surfaces under ORR conditions. Remarkably, elements like Cr, Mo and Ir can form stable hydroxide 0d and 2d structures on Pt and can resist dissolution by preferentially covering the Pt edge and kink sites, which are otherwise susceptible to degradation. These nanoscale structures exhibit properties different from their bulk counterparts and can effectively tune the reactivity of the surface by introducing an inhomogeneous strain field into the Pt terrace sites.

The overarching goal of this dissertation is to formulate design principles applicable to metal nanoparticle catalysts coated with surface oxides. Given the pivotal role of the systems in industrially significant catalysts, the development of strategies aimed at engineering novel active sites using surface oxides is of great importance. The comprehensive molecular-level understanding of metal-metal oxide interactions, established through these studies, thus serves as a foundation for the study of these effects across a wider spectrum of reactions beyond ORR and CO oxidation. Through such studies, combined with rigorous experimental confirmation, it may ultimately be possible to engineer new classes of metal/oxide interfaces for desired catalytic applications.