Ghanekar Thesis Defense

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Throughout history, emergent technologies have become possible due to discovery, synthesis, and access to improved materials. Heterogeneous catalysts, which are the bedrock of the modern chemical industry, are no exception. Advances in catalyst research have resulted in wide-ranging applications from energy production and storage, to the synthesis of fine chemicals and drug discovery. Now, more than ever, discovering next-generation catalysts is crucial as we work towards a carbon-neutral and sustainable economy.

That said, heterogeneous catalytic reactions are shown to be sensitive to the atomic-scale complexities arising under *in-operando* conditions, such as variations in surface morphology, composition, and adsorbate-adsorbate interactions. To understand the subtle interplay of these diverse phenomena, it is necessary to develop an atomic-scale representation of the catalyst under the reaction conditions. In that spirit, understanding what makes the catalyst "active" and stable is vital to tease out the insights, and develop principles that lay the groundwork for material discovery. Understanding the molecular-level behavior of materials has been the focus of my doctoral research. Through a combination of atomic-scale simulations, machine learning, spectroscopy, and chemical kinetics we have explored the active sites and reaction mechanism for reactions relevant to energy generation, with hopes of opening up exciting possibilities for rational design of structurally complex and ubiquitous catalysts.

In this talk, we first explore the effects of complex metal/oxide interfaces, molecular adsorbates, and possible heteroatom dopants on the Water-Gas Shift reaction (WGSR). A lattice-matched platinum (Pt) on magnesium oxide (MgO) model is developed to understand the effect of the metal/oxide interface. Special care is taken to ensure a reasonable representation of real-life catalyst is preserved by mitigating anomalous interfacial strain or disparate size-effects. The insights gained from the electronic structure relaxations, reactor modeling, and chemical kinetics are used to construct a closed-form kinetic expression to identify thermodynamically and kinetically sensitive steps. The mechanistic and reactivity insights gained from these analyses form a strong basis for identifying reactivity descriptors at the metal/oxide interfaces.

Further, the presence of numerous atomic-scale configurations, and the difficulty in systematically generating and analyzing the surface representations, make atomic-model development non-trivial. To address this challenge, a graph network-based enumeration and prediction strategy is explored. We discuss the Adsorbate Chemical-Environment based

Graph Convolution Neural Network (ACE-GCN), a versatile framework with the ability to encode atomic configurations comprising diverse adsorbates, binding locations, coordination environments, and variations in the substrate morphology. This workflow is used to generate and rank surface adsorbate configurations for reactions which are shown to be affected by the presence of high adsorbate surface coverage. We demonstrate the utility of the workflow to determine relevant configurations for the case of high-coverage adsorbates on Pt_3Sn and Pt-steps surfaces.

The atomic-scale catalyst models and computation tools proposed through this work can serve as a starting point for developing a detailed description of complex catalyst surfaces under *in-operando* conditions, ultimately aiding to unravel the factors that govern their functioning in chemically complex environments.