The modification of metal active sites in catalysts has garnered a lot of attention as a research area. While metal catalysts have long been used for a variety of reactions, being able to tune metal active sites by either adding other metals (alloys) or non-metal elements (oxides, hydrides, phosphides, etc.) opens opportunities to improve the selectivity and activity for these reactions. Furthermore, additional reaction pathways may become accessible as catalyst properties are adjusted. Here, I investigate metal-based catalysts that are improved in some capacity by the addition of another element.

First, I study the shift in selectivity for hindered C–O cleavage in biomass derived oxygenates when phosphorous is added to pure metal catalysts. Specifically, I look to understand how P modifies the metal active sites to improve this selectivity. It was shown in a prior study that the addition of P to Ni shifts the selectivity such that the hindered C–O cleavage in MTHF becomes the preferred reaction over unhindered C–O activation. However, what was not understood was the role P plays in causing this shift in selectivity. Using DFT calculations we show that when moving to other transition metals (except for Ru), the addition of P similarly increases the selectivity for hindered C–O cleavage. These shifts in selectivity can generally be correlated to the charge on the metal atoms as the more positive metal atoms tend to be more selective for hindered C–O activation.

I then study the structure of AuPd particles and work to develop a model to predict exchange energies for these particles. Initial exchange energy calculations suggest that Pd prefers to be in the subsurface of Au and isolated from itself, agreeing with previous findings in literature. Additionally, we observed a nonlinear trend with exchange energies as we reached higher Pd compositions which we were able to correlate with the Fermi energies of the particles. The model developed from these calculations was then implemented within a Monte Carlo tool to predict the most stable structures across a variety of Pd compositions. These AuPd particles have been shown to restructure in the presence of adsorbates, particularly CO*. Therefore, I also investigate what this restructuring might look like and what the most stable configurations of Pd and CO* are at dilute compositions of Pd.

Kinetics are also heavily influenced by what adsorbates are present on your surface. So as the final part of this work, I probe the adsorption of H* on pure metal nanoparticles in an attempt to understand how each metal binds H* and at what coverage saturation is reached. In all cases, saturation coverages exceed the often-assumed saturation coverage of 1 ML. This study also

accounts for the formation of hydride-like structures and how saturation coverages change with particle size.