Fundamental Studies of d-Band Transition Metal Alloys

BY

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THESIS

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This thesis is dedicated to my family, whom has supported my decisions unconditionally and has been there throughout my life. Without them I would have never gotten this far.
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<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>BCC</td>
<td>Body centered cubic</td>
</tr>
<tr>
<td>CN</td>
<td>Coordination number</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
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<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
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<tr>
<td>FCC</td>
<td>Face centered cubic</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized gradient approximation</td>
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<td>HCP</td>
<td>Hexagonal close-packed</td>
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<td>HREELS</td>
<td>High resolution electron energy loss spectroscopy</td>
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<td>IR</td>
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<td>MD</td>
<td>Molecular dynamics</td>
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<td>ML</td>
<td>Monolayer</td>
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<td>STEM</td>
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This thesis will attempt to make some small contribution toward our understanding of how particle size effects, alloy effects and support effects impact the performance of heterogeneous catalysis. As a starting point, in chapter 2, we have examined the reverse spillover of hydrogen on Rh₆ clusters using density functional theory over a variety of supports: TiO₂, Al₂O₃, MgO, SiO₂ and a LTA zeolite. In this work we attempt to elucidate how the identity of the support influences the presence of hydrogen on the metal cluster. While no universal descriptor of reverse spillover was identified, the support does have a strong influence on the thermodynamics of reverse hydrogen spillover. We have also examined alloying in heterogeneous catalysts. Through alloying one may manipulate the properties of a catalyst, thus creating highly selective materials that are of high interest to the industrial processes. Combining X-ray absorption spectroscopy and density functional theory calculations, Chapter 3 examines trends in the simulated X-ray Absorption Near Edge Structure (XANES) of bulk alloys.
of Pd with other late transition metals and relates the observed changes in the XANES upon alloying to features in the valence electronic states of these materials. We find that effects can be grouped into three categories: 1) changes in M-M bond distances 2) changes in bond overlap due to differing orbital extents and 3) charge transfer effects. When synthesizing alloy nanoparticles, not all systems form homogeneous structures. In fact, there are many prominent instances of segregation where the shell becomes enriched in one metal and the core is enriched in the other. These so-called core-shell alloys often display unique behavior which lies outside the range of behavior of the monometallic components. In chapter 4, we use a simple model to explain the changes in the electron density of states in these core-shell systems for a variety of combinations of late d-band transition metals. Chapter 5 introduces a method based upon changes in the XANES (combined with IR) for characterizing the surface composition of bimetallic nanoparticles. In chapter 5 we focus upon our contribution to that work which involved the calculation of CO adsorption on a variety of PdPt alloy surfaces which aided in understanding the observed spectra. Finally, using acrolein hydrogenation as a test reaction, chapter 6 examines how the presence of an alloying metal influences both the kinetics and thermodynamics of the complete mechanism. In addition, we have investigated the influence of nanoparticle structure on the observed reactivity and selectivity.
1. **INTRODUCTION**

1.1 **Motivation**

Heterogeneous catalysts, typically involving transition metal nanoparticles supported on high surface area inert substrates, are used in 90% of processes in industrial commodity chemicals manufacturing (1). The high catalytic activity of transition metals in many reactions has been attributed to their partially unoccupied d-electron states (2). However, the possibility to tune the catalyst performance and improve its desired properties relies on developing a detailed understanding of how the catalyst functions. In this thesis we will seek to explore issues surrounding the electronic structure of heterogeneous catalyst including alloying, support effects and particle size effects. We have focused on the use of density functional theory to examine these issues in a series of disparate projects. Chapter 2 will explore the phenomenon of reverse spillover of hydrogen from the metal oxide support to a Rh₆ cluster. In chapter 3, an analysis of the effect of alloying Pd with different late d-band transition metals on the x-ray absorption near edge spectra, and its relation with the position of the d-band center, will be presented for bulk alloys. However, nanoparticles often lack homogeneity and sometimes form core/shell structures with enrichment of one metal at the surface. In chapter 4 we explore how the electronic structure of these alloys compares with the bulk alloys in chapter 3 through an examination of the density of states and XANES for single monolayer and
bilayer surface shells. Chapter 5 looks into adsorption of CO on Pd, Pt and PdPt alloy nanoparticles as a probe for understanding changes in reactivity for neopentane hydrogenolysis. DFT based vibrational frequency calculations are used to aid in understanding corresponding infrared spectroscopy experiments and allow for determination of structures at high CO coverages. Of course, the true measure of the effect of alloying manifests itself via changes in observed reactivity. In chapter 6, density functional theory calculations are used to compare different reaction paths for the selective hydrogenation of acrolein over Ag and AgIn alloy surfaces ($\text{Ag}_3\text{In}(111)$ and $\text{AgIn}_2(110)$). In addition, the effect of particle size is explored via DFT calculations of acrolein hydrogenation on $\text{Ag}(221)$ as a model for a smaller nanoparticle with more step edges.

1.2  \textit{d-band theory}

The fundamental properties of $d$-band transition metals have been studied extensively by Norskov and coworkers using Density Functional Theory (3). In their pioneering study, Norskov and Hammer proposed that CO chemisorption can be understood using a simple model describing the CO electronic states and the $d$-band valence of the transition metal. Their work demonstrated that a trend in the adsorption behavior could be developed relating the strength of adsorption to the energy of the $d$-band center with respect to the Fermi level.
The interaction of CO with a Pt surface is illustrated in Figure 1. Norskov et al. proposed a two step model in which the adsorbate’s electronic levels couple with the sp levels of the metal first causing a broadening and a renormalization of the energy. Then a second step involves the interaction of the renormalized adsorbate’s electronic levels and the metal’s d-band causing a splitting of the adsorbate’s levels into bonding and antibonding levels. Since the sp bands of d-band transition metals are relatively similar, the position of the d-band center with respect to the Fermi level is the critical factor which determines the strength of the interaction of the metal with the adsorbate. In relation to the Fermi level, a downshift in the d-band center of the metal implies a more stable structure, thus, less reactive. An opposite effect occurs when the d-band center shifts up towards the Fermi level resulting in a more reactive
metal. A simple model of adsorption of CO on a wide variety of late transition metal surfaces using a single parameter, the $d$-band center, gave good agreement when compared to a full Density Functional Theory calculation as in shown in Figure 2 (3). The model also captures the shifts in the CO chemisorption energies from single crystal surfaces to overlayer structures as shown by the dashed lines in Figure 2.

Figure 2 Comparison of d-band model and full DFT-GGA chemisorption energies for different metal systems (3).
Weinert and Watson show that the variation in surface core level shifts for metal overlayers is accompanied by a similar shift in the center of gravity of the $d$-bands (5). Comparing experimental core-level spectroscopy shifts with computational simulations, an explanation of the experimental shifts was offered by separating contributions to the shifts using a spherical decomposition model on bulk alloys as well as pseudomorphic overlayers. For bulk alloys, the trends of the shift signs are correlated to the changes in the $d$-band counts. On the other hand, shifts in the overlayer systems are not only related to $d$-band contributions but also to Coulombic interactions. These Coulombic interaction energies were divided into intra and extra-atomic contributions being the latter the dominant effect in determining the sign of the shift. Intra-atomic difference between bulk alloys and adlayers was found to be primarily due to the difference in behavior of their $s$ electrons (5).

Again using a CO as a test molecule, Hammer et al. also studied the effect of structure on the $d$-band center (4) showing that coordination number has a direct effect on the $d$-band center location with respect to the Fermi level. Overcoordination results in increased $d$-band overlap resulting in a low reactivity of the structure, and accordingly, an undercoordination of atoms results in a less crowded $d$-band, increasing reactivity. This can be explained by a rectangular $d$-band model, where the overall width of the $d$-band either contracts or expands to maintain constant electron filling of the band.
Expansion of the $d$-band following the rectangular model will cause the center of the $d$-band to upshift away from the Fermi, contrary effect will happen when the $d$-band undergoes contraction, where a compensation effect will shift the center towards the Fermi. Figure 3 shows an upshift of the $d$-band center as the coordination number of the atom decreases from a terrace to a step to a kink. One question that arises after considering elemental identity, structure of the slab and overlayers is: Does the $d$-band center model apply to other adsorbates besides CO? Greeley and Norskov studied the oxygen binding on binary transition metal surface alloys using DFT calculations (6). Using a ABCD notation, where A,B and C are atoms in the surface layer and D is the subsurface layer, Greeley and Norskov modeled over 700 number of
alloys systems concluding that oxygen binding to the studied systems can also be described by the single parameter of the $d$-band theory as shown in Figure 4. Also, they demonstrated the dependence of the oxygen binding energies on the position of the $d$-band center as their results show that for noble metals this binding energy is weak than for other transition metals, caused in part by the filled $d$-bands of the noble metals. Exceptions in Figure 4 primarily involve structures containing Fe. Magnetic effects were not taken into account in this calculation, which partially explains these outliers. Strain might also play a role in the case of outliers on Figure 4 since Fe is a bcc unlike the other metals in this study which are fcc or hcp. Deviations of the data containing noble metals are partially explained by the greater scattering in the correlations between the $d$-band and binding energy shifts that are typically associated with noble metals on surfaces due to the complete filling of the $d$-band. This has recently been explained by Linic and co-workers (7) as a result of the complete filling of anti-bonding orbitals formed between highly electronegative adsorbates and metals with full or nearly full $d$-bands as explained later in the surface alloy section.
Density Functional Theory based calculations have been shown to be a powerful predictive tool. Although the accuracy of DFT is not to the point of predicting reaction rates precisely, it has the potential of predicting trends when comparing different materials. An example of this is the work performed by Norskov on ammonia synthesis (8) (9). For an elementary reaction, a linear relationship between the activation energy and the reaction energy has been shown to be true for any “late” transition state (i.e. the transition state structure has commonality with the product structure). This relationship, called the Bronsted-Evans-Polanyi relation (BEP), has been exploited by Norskov and co-workers to reduce the
computational load (i.e. avoid explicit calculation of all barriers) in their efforts toward rational catalyst design (8). For example, ammonia synthesis follows a BEP relation and thus is generally accepted that its synthesis follows elementary steps in which both molecules, \( \text{N}_2 \) and \( \text{H}_2 \) adsorb onto the surface and dissociate. Dissociated hydrogen then attaches to the nitrogen atom in a stepwise manner by forming \( \text{NH} \), \( \text{NH}_2 \) and finally \( \text{NH}_3 \) that desorbs from the surface (10). Industrially, a promoted iron catalyst is used, and it has been established that there is a pressure dependence for this reaction (11). It would be ideal to be able to predict the catalyst behavior at industrial operation conditions. With this goal in mind, Norskov proposed a modeling method for ammonia synthesis based on the reaction mechanism proposed by Ertl, in which the rate limiting step is the dissociation of nitrogen on the surface (12). The dissociation of nitrogen is correlated with the nitrogen binding energy, via a BEP relationship and therefore it is possible to predict turnover frequencies based on this one (N binding energy) parameter (9). With this in mind, Norskov et al. proceeded to simulate the volcano plot on different metals as seen in Figure 5 (9). Although the experimental data does not lie exactly on the line predicted by the model, the correct trend is established (note that the model assumes that the coverage of N is the same on all surfaces- this is clearly not true). The volcano plot shows as the most efficient catalysts for ammonia synthesis to be iron and ruthenium. For the conditions used in the calculation (0.8 bar, 588 K, \( \text{H}_2:\text{N}_2 = 3 \)), it is clear that the optimal catalyst would be between Fe and Ru which coincides with the industrial catalysts used (promoted Fe) (8). Norskov’s volcano plot for ammonia synthesis is an excellent example of how by using adsorbate binding energy as a modeling parameter, we can potentially optimize catalysts. For a
specific reaction, one could envision the use of the d-band center as a predictive parameter to determine the optimal catalyst and further improvement by alloying.

![Figure 5 N₂ dissociation volcano plot (9).](image)

1.3 **Alloy Effects**

As mentioned above, the d-band model works well for a large variety of alloys. However, in order to understand alloy properties, one would like to understand the origin of the d-band center shifts in alloys. Alloying alters the structure and composition of a catalyst
usually giving it intermediate properties between those of the pure components. However, alloys may also possess unique properties leading to behavior that falls outside of the range between the pure components. Based on a recent review by Axel Gross, an explanation of various effects that contribute to the diverse behavior of alloys will be given (13).

Figure 6 Representation of a surface alloy.

Important parameters in the activity of a catalyst are ensemble effects and ligand effects. The electronic interactions between the components of the alloy are referred to ligand effects. Ligand effects can be further subdivided into electronic effects and geometric effects. Electronic effects are related to the changes in the bonding when one metal is substituted for
another. Geometric effects are related to the changes in equilibrium bond distances when metals are alloyed. Modification of interatomic distances in bimetallic systems can have also an effect on catalytic activity, therefore geometric effects are important as a component of ligand effects as well. In addition, for many reactions a particular number of sites is required for the reaction to take place, this is denominated as an *ensemble effect*.

### 1.3.1 Surface Alloys

Homogeneous alloys in which the surface composition mirrors that of the bulk are designated by Gross as surface alloys (13). The surface alloy will have both elements present in the surface layer and therefore the nature of the surface alloy opens the possibility of a multifunctional catalyst, where each metal present has a different function (i.e. each one might adsorb different reactants needed for a particular reaction to occur).

A bifunctional catalyst that has been studied by Shubina and Koper (14) is a PtSn alloy. On the Pt₃Sn(111) surface, CO shows a preference for Pt but OH has an affinity for Sn, thus giving this catalyst a selectivity for this type of reaction for aqueous CO oxidation (effectively water gas shift). Using DFT calculations Shubina and Koper use the energy of adsorption of CO and OH onto PtRu, PtMo and PtSn based alloys to propose an improvement to the PtRu catalysts by using a metal (Sn) that does not have an affinity for CO but which will adsorb water (and OH) preferentially on atop sites (14).

It should be mentioned that materials that are immiscible in the bulk may still be able to form alloys at the surface and at the nanoscale (15). Therefore, when searching for alloy
combinations that will serve as improved catalysts, many options are available due to the length scales at which catalysts operate. Another example of improvement by alloying is given by Besenbacher et al. for Ni steam reforming catalysts. Ni catalysts are used in methane steam reforming but suffer from deactivation due to coking. In their combined experimental and theoretical work, Besenbacher and co-workers, propose the design of a more effective catalyst by alloying Ni with Au. Although Au and Ni are immiscible in the bulk, it is possible to form an alloy at a surface level as seen in the STM images (shown in Figure 7) of gold deposited on Ni(111).
In the images, the dark spots are Au whereas the Ni atoms show up as bright protrusions. It is also observed that the Ni atoms near the Au have a different contrast than Ni away from the Au due to changes in the electronic structure that the Ni undergoes by neighboring with Au. The AuNi catalyst is also a good example of a system with ensemble effects. Au acts as a spacer hindering C-C bond formation and thereby preventing coke formation. AuNi catalysts do possess a higher barrier for the dissociation of CH$_4$ to CH$_3$+H. However, the small decrease in reactivity (the barrier increases by 0.17 eV if one Au neighbor exists compared to Ni(111)) is viable given the improvement in catalyst lifetime (15).
1.3.2 **Pseudomorphic overlayers**

Pseudomorphic overlayers refer to a thin or monolayer of a metal supported on a slab of a different metal known as the host. These systems are also sometimes referred to as core/shell alloys. These systems demonstrate unique characteristics as a combination of geometric effects which result from the fact that the overlayer will retain the same lattice constant as the underlying host and electronic effects stemming from the bonding between the host metal and the overlayer. For these systems it is important to take into account the number of layers of the shell above the core metal, as the electronic effect dies out quickly as layers are added to the shell. For thicker shells (> 4 layers) geometric effects may still be present and are dominant with respect to electronic effects (16).

Figure 8 Representation of pseudomorphic overlayers.
The Pt/Ru system is of interest in the field of CO tolerant fuel cell catalysts as it has been shown to reduce the binding of CO to surface. Electro-oxidation of CO is important on fuel cell systems due to the poisoning of adsorbed CO if unreacted. Starting with methanol as a fuel source, the anode reaction produces \( \text{CO}_2 + 2\text{H}^+ \). However, the intermediate products, mainly CO, may poison the Pt surface, thus making it imperative to weaken the adsorption of CO onto the surface in order to create a viable long lasting fuel cell (17) (18) (19). Alloying Pt with Ru has been shown to prevent strongly bound CO from poisoning the surface by weakening the binding energy of CO (20).

The lattice constant of Ru is 2.5% smaller than the Pt lattice constant. Under this contraction, Pt layers maintain pseudomorphic epitaxial up to at least 4 layers. The explanation of the reduced reactivity of the Pt/Ru system as compared to monometallic Pt can be explained in terms of \( d \)-band theory. Compression of the Pt atoms results in an increased overlap of the \( d \)-band which causes a downshift in the \( d \)-band center with respect to the Fermi level. In addition, interaction with Ru host makes the Pt less reactive as Ru can effectively steal charge from the Pt. Therefore, both geometric and electronic effects result in a downshift of the \( d \)-band center making this system less reactive when compared to Pt.

In order to distinguish between geometric and electronic effects in CO adsorption, DFT calculations were used to examine the adsorption of CO on single (unsupported) layers of Pt(111). In this case the lack of a second metal eliminates the electronic effect from rehybridization. It can be clearly observed in Figure 9 (by following the continuous line), that the primary effect in changes in CO adsorption for pseudomorphic monolayer catalysts is
geometric. However, for the particular case of Pt/Ru the adsorption energy change is greater than that predicted by the curve based on geometric effects alone, revealing an electronic ligand effect is also present.

As seen in Figure 9 the system Pt/Au is the lowest in change, in fact the change is negative, and in contrast with the Pt/Ru system, adsorption of CO on Pt/Au is stronger as the lattice undergoes significant expansion, shifting the $d$-band center towards the Fermi edge. The upshift of the $d$-band center is a result of an unstable Pt surface structure that then eagerly reacts to stabilize itself.

Figure 9 Calculated change in CO adsorption energy with respect to CO/Pt as a function of Pt-Pt distance (13).
In the case where another relatively inert metal is used as a host, but instead of expansion there is a compression, the geometric effect and the electronic effect will counteract each other. For example, Pd/Cu systems, where Cu is an inert metal with a lattice constant 8% smaller than the one of Pd (The extreme strain of a Pt overlayer on Cu, a similar case to PdCu, in fact does not exist (21). The Cu/Pd(111) system on the other hand has been found to be possible to produce in a layer by layer fashion for at least the first two layers (22). Both Cu/Pd(111) and Pd/Cu(111) systems have an intermediate behavior between pure Cu and pure Pd.

Electronic effects in this case result in a stronger Cu-Pd interaction compared to Cu-Cu. In fact the model shows the Pd atoms are bound to Cu(111) stronger by 0.3 eV than Cu atoms which then reflects on the lower hydrogen binding energies when compared to pure Pd. This interaction Cu-Pd on both systems gives it intermediate characteristics between the pure metals. The influence of lattice mismatch is more noticeable in the Pd/Cu(111) and less important in the Cu/Pd(111) as seen in Figure 10. In the latter case, CO binds weakly to both Cu and Cu/Pd(111). While strain effects would suggest that Cu/Pd(111) should bind CO more strongly than Cu(111), charge transfer from Cu to Pd reduces its reactivity and the binding is weakened.
1.3.3 Supported particles

Support effects are also a key factor in nanoparticles catalysts. The reactivity of the support may have a direct impact in the shift of the d-band center of the atoms of that first layer in contact with it, but has a less noticeable impact on second nearest neighbors. Coordination of the nanoparticles plays an important role in the heightened activity. Using water gas shift reaction, Ribeiro et al. demonstrate the importance of coordination of the metal atoms by studying Au supported nanoparticles (23). First, it was determined that the atoms with lowest coordination number, were the dominant active sites for the water gas shift reaction. Hence, smaller particle sizes are crucial for the increase in corner sites for the WGS reaction (23). Later, the support was shown to play an important role in the WGS reaction by
activating the water molecules. By studying Au nanoparticles on Al$_2$O$_3$ and TiO$_2$, Ribeiro et al. showed the support increases the reaction rate by a factor of 20 when changed to TiO$_2$ (24). The authors hypothesize that the support is no longer inert. The support effect is not due to electronic changes in the Au nanoparticles. Instead, the support serves as a capture zone for H$_2$O which is shuttled to the nanoparticle/support interface. This concept of spillover from either the metal to the support or the support to the metal nanoparticle will be explored in chapter 2 with a completely different example showing the movement of hydrogen from one reservoir to another.

1.4 Exceptions to the d-band model

Although the d-band center model seems to work very well for a wide range of alloys, there are exceptions. Xin and Linic have recently demonstrated that for Pt and Pd skin alloys where Pd and Pt are placed above 3d metals, there is a reversible effect in the adsorption energy trends for highly electronegative adsorbates like OH (7). In their case study of OH adsorption on skin alloys, interaction between the sp-band of the support governs the strength and length of the bond. On the other hand, orthogonalization between the renormalized adsorbate state and the metal d-state results in repulsion. Electron transfer from the subsurface guest to the host depends on the electronegativity of the metal in the sublayer. The alloys with sub-surface layers on the left of the periodic table, which have more electronegativity difference with the top layer of Pd or Pt, will have increased electron transfer to the surface thus making the surface ‘reject’ the adsorbate creating longer bond lengths to reach a stable state. This long bond distance causes the orthogonalization of the renormalized
*sp* splitted levels and the *d level* to be smaller and resulting in a weaker Pauli repulsion and thereby stronger adsorption of the OH molecules. Therefore, the higher *d*-band of the skin alloy metal results in the adsorbate to be bound less strongly (7).

This situation described by Xin and Linic occurs only in systems with nearly fully occupied *d*-band and with adsorbates with almost completely filled valence shells (for example, the adsorption of O which is less electron rich than the O atom of OH, follows typical *d*-band model behavior).

In addition to the examples cited above, another class of bimetallic systems which may deviate from the well-established *d*-band correlations of Norskov, would be alloys involving main group metals with *d*-band transition metals. In this case, a *d*-band transition metal is alloyed with a metal whose *d*-band is fully filled and therefore its valence electrons at the Fermi level are primarily of *p* character. This suggests that a new set of rules must be established to understand these alloys which we designate as *p*-*d* alloys. There are already a few examples of *p*-*d* alloy catalysts that demonstrate their utility. For example, the high selectivity of Pt-based catalysts in the process of hydrogen generation by catalytic reforming of oxygenated hydrocarbons in aqueous phases has been studied by Dumesic *et al.* (25). More recently, Dumesic and co-workers found that R-NiSn (Raney-NiSn) catalysts possessed similar activity and selectivity as compared to Pt (26) giving an example of possible replacement of costly catalysts with less expensive ones achieved by alloying.

Young-Ki *et al.* studied the deposition of Sn over Pt (111) using different Sn coverages (27). It was concluded that adsorption of tin on Pt(111) reduces the surface tendency to
deactivate by coking when less than 0.2 monolayers of Sn are present. Another study by Yarusov showed the positive effects of Pt-Sn catalysts in a dehydrogenation of propane to propene reaction with a selectivity of 96-99% (28). Correlations of the conversion of propane and the fraction of Pt in a Pt-Sn alloy have been examined by Bednarova et al. It was shown that activity was incremented with higher content of Pt in the catalyst, however, some Sn is necessary to increase the stability of the catalyst (29). PdZn is another popular example of this type of p-d alloy catalyst. Iwasa et al. found that correlating their XPS (Figure 11) results to catalytic activity for steam reforming of methanol, that alloy formation (above 573 K) was necessary for a selective catalyst (30).

All the previous studies show the benefits of alloying but there is no detailed explanation for the electronic effects happening by the formation of these alloys. A systematic evaluation of these systems, bringing together experimental and theoretical input is critical to produce a new generation of catalysts with tunable properties and greater selectivity and improved resistance to deactivation.
In addition to experimental studies of p-d alloys, theoretical studies on these systems have been performed to explain their improved catalytic function. PdZn is a popular choice due to its demonstrated ability to serve as a methanol reforming catalyst. It has a tetragonal structure and PdZn(111) is the lowest energy surface. Rosch et al. performed DFT calculations to compare the electronic structure and reactivity of Cu(111) and PdZn(111) surfaces. They concluded that PdZn (111) and Cu(111) surfaces have very similar d-density of states profiles as
shown in Figure 12 (31). The electronic structure of PdZn resembles that of Cu, giving it similar properties for adsorption behavior. A Cu based catalyst is used in industry for water gas shift, but it sinters at high temperatures. The similarities in the DOS profiles of PdZn and Cu hint that one could replace Cu with PdZn to improve thermal stability (although it is a more expensive catalyst). This type of analogy where one could replace a catalyst with a less expensive or more efficient one is the concept driving our research direction.
Figure 12 Calculated DOS profile. a) - - - Bulk Pd — PdZn. b) - - - bulk Pt — PtZn. c) 3d-band of bulk Cu (31).

Experimental and computational techniques will be required to create a predictive model to describe adsorption tendencies in p-d metal alloys as well to understand the influence of alloying on the X-ray absorption near edge spectra. An explanation of the techniques used is given in the next section.
1.5 X-Ray Absorption Spectroscopy (XAS)

One of the primary techniques that can be used to understand the electronic structure of bimetallic nanoparticles is X-ray Absorption Spectroscopy. XAS is highly useful in that it can impart information about both the physical geometry as well as the local electronic environment of the catalyst. As shown in Figure 13, XAS can be divided into two parts: X-Ray Absorption Near Edge Structure (XANES) and Extended X-Ray Absorption Fine Structure (EXAFS) (32). The former will give information about the absorbing atom of interest while the latter will give information about the neighboring atoms.

This technique requires a monochromatic source with high intensity that can only be found at synchrotron facilities around the world. The experiment can be performed in either a transmission mode or fluorescence mode. A peak in the absorption of the x-rays by the sample will be observed when the photon energy is sufficiently high to eject an electron from the core and it subsequently scatters to the valence region. The electron wave leaving the originating atom comes in contact with other atoms that are near it (presumably those that are bound to it in the molecule) resulting in scattering of the ejected photoelectron. The scattered photoelectron interference can be detected and measured and yields information about the location and distance between atoms within a molecule (33) (34).

XAS is element, oxidation state, and symmetry specific technique making it a precise tool for structural characterization of supported metal catalysts. This information can be used to understand the structure of alloy catalysts as well as giving information about how alloying perturbs the electronic structure.
A critical issue in XAS is the analysis of the spectra. Data analysis can be done with different software available, including, Athena (35) and WinXAS (36). Both the XANES and EXAFS regions must be fit and compared to reference materials. References will be done either experimentally or computer aided as available in the Athena database, but experimental references are preferred. Normalization of all raw data will be done using polynomial fits. After normalization, energy of the edge will be subtracted and data will be converted from energy to photoelectron momentum and a cubic spline fit will be performed. Different k weightings will be used to confirm that the answer does not change and it is fit appropriately to higher k-weighing. A Fourier Transform is then taken of the normalized data and, using amplitude and
phase data from references, spectra fits of the transformed data are made allowing extraction of both coordination numbers and bond distances.

1.6 **Density Functional Theory Calculations**

The primary computational approach that will be used in this thesis is Density Functional Theory (DFT). DFT calculations will be done using Vienna Ab-initio Simulation Package (VASP) (37) (38) (39) (40). DFT is a quantum mechanical theory used in physics and chemistry to investigate the ground state of many-body systems, in particular atoms, molecules and the condensed phase and has proven to be quite useful in the analysis of the electronic structure of bulk materials and surfaces.

Traditional methods in electronic structure theory, in particular Hartree-Fock theory and its derivatives, are based on the wavefunction. The main objective of density functional theory is to replace the many-body electronic wavefunction with the electronic density as the basic quantity. Whereas the wavefunction is dependent on 3N variables, three spatial variables for each of the N electrons, the density is only a function of three variables and is a simpler quantity to deal with both conceptually and practically. Hohenberg and Kohn proved that the total energy, including exchange and correlation, of an electron gas (even in the presence of a static external potential) is a unique functional of the electron density (41). The minimum value of the total energy functional is the ground-state energy of the system and the density that yields that minimum value is the exact single particle ground-state density.
The Kohn-Sham total-energy functional (42) for a set of doubly occupied electronic states \( \psi_i \) can be written as:

\[
E[\{\psi_i\}] = 2 \sum_i |\psi_i|^2 \left[ \frac{\hbar^2}{2m} \nabla^2 \psi_i + \int V_{ion}(r)n(r) dr + \frac{e^2}{2} \int \frac{n(r)n(r')}{|r-r'|} \, d^3r ight] + E_{XC}[n(r)] + E_{ion}(\{R_i\})
\]

Equation 1 Total-energy functional

\( E_{ion} \) is the Coulomb energy associated with interactions among nuclei at positions \( \{R_i\} \)

\( V_{ion} \) is the static total electron-ion potential

\( n(r) \) is the electronic density given by

\[
n(r) = 2 \sum_i |\psi_i(r)|^2
\]

\( E_{XC}[n(r)] \) is the exchange-correlation functional.
Experimental investigations in heterogeneous catalysis often raise questions that cannot be easily answered by the experiments themselves. In such a situation it is sometimes possible to explain experimental results using insights derived from DFT calculations (43; 44; 45; 46). DFT offers a method of investigating atomic level models and consequently the potential to develop a detailed, fundamental understanding of the factors that influence the chemical reactivity of surfaces.

The calculations will be performed using a plane wave basis set and projector augmented wave pseudopotentials of Blochl with periodic supercells (47) (48). Exchange and correlation energies will be calculated using the Perdew-Wang ’91 form (PW91) (49) (50) of the generalized gradient approximation and the Perdew-Burke-Ernzerhof (PBE-GGA) functional (51) (52). Geometries will be considered to be optimized when the forces are within a convergence tolerance of 0.025 eV/Å.

In addition to the VASP code, the CASTEP code, in particular the modules for evaluating electron energy loss spectroscopy (EELS) and calculating the density of states (DOS), is used. EELS is similar to XANES, only now instead of using a photon, an electron is used to trigger the resonant electron ejection from a core state. CASTEP possesses a module which allows for simulation of an EELS (XANES) spectra based on overlap integral of the core state and the final state (53) (54) (55). The core state is evaluated using an all electron calculation of an isolated atom, whereas the pseudowavefunction for the final state is generated by an ultrasoft pseudopotential calculation within CASTEP. Gaussian broadening of 0.2 eV was applied to mimic the instrument broadening and the effect of smearing due to the finite lifetimes of the final states and fact that calculations necessarily involve a finite number of k-points. A more
detailed discussion of the key consideration for calculating the ELNES using CASTEP, and a comparison of the CASTEP pseudopotential DFT code with the all electron code Wien2k is provided by Seaborne (56).

The DOS module allows for calculation of the electron energy levels and their occupations with the ability to resolve the electron density into s, p, d or f orbitals based on symmetry (i.e. fits of the electron density into spherical harmonics). The DOS calculations in combination with a partitioning of charge into Bader surfaces allows for us to monitor changes in the filling of the orbitals and the transfer of charge between neighboring atoms. It will be of special interest to monitor changes on the d-band center due to support effects and alloy effects discussed in this work.

To further understand the behavior of d-band metals when alloyed we started a strategic study by modeling palladium alloyed with different elements. The goal is to elucidate a trend as the alloyed metal is moved across and up and down the periodic table of elements.

The main objective as stated before is to develop an understanding of the relationship between alloying and reactivity to predict the properties of the alloy. Our strategy is to use X-ray absorption spectroscopy (specifically XANES) as the primary tool to “measure” the electronic structure of the alloys that are synthesized and then to compare the experimental XANES to our simulated spectra (with accompanying PDOS plots) to advance our understanding. As a start, models for the PdX alloys (X = Co, Ni, Cu, Zn, Ga, Ge, Rh, Ag, Ir, Pt, Au) containing the colored elements shown in Figure 14 have been constructed and optimized.

To this point, we can say that the perturbations in the d-band due to alloying fall into two categories: 1) changes in the lattice lead to large strain effects that modify the degree of
bonding. 2) changes in orbital extent which change the hybridization of bonding without large lattice shifts.

Our DFT work on alloys has also contributed to the explanation of CO bonding to Pd-Pt alloys. Turn over frequency is an important measurement when it comes to reaction kinetics. On bimetallic alloys, the difficulty arises when both metals adsorb the gas molecule that is being used to determine the active adsorption site in techniques such as chemisorption or infrared spectroscopy. Wu et al. have developed a method to interpret vibration frequencies of alloys of this type in which both adsorb CO with the combination of DRIFTS and XANES (57). By assuming a simple model of (111) surfaces of Pd, Pt, and PdPt bimetallic, adsorption energy and vibrational frequencies are also calculated using VASP. It is clear that the model is a rough approximation to the real nanoparticle and therefore complete agreement is not expected. Chapter 5 shows the comparison between experimental data available for different coverages of CO on Pd and Pt as well as a proposed structure for the bimetallic PdPt based on the single metal preferred adsorption sites. Using d-band theory, we are able to explain the trend of the adsorption event when compared to monometallic surfaces. Density of states profiles simulated using CASTEP are provided as an example of how the Hammer and Norskov model works for this case.
1.7 Selective Acrolein Hydrogenation as a Model Reaction

In the course of this investigation, it is important to link changes in the electronic structure of the alloy materials to actual catalytic activity. In this case, we have chosen to focus on a particular reaction of some industrial interest: the selective hydrogenation of acrolein to allyl alcohol. Selective hydrogenation of acrolein is not only of special interest for the production of fine chemicals for use in perfumes but also as precursors in the pharmaceutical industry (58) (59). Furthermore it is of more general interest because it poses a selectivity challenge which can be applied to a broader spectrum of selective hydrogenation reactions. Acrolein is the C3 unsaturated aldehyde and can be hydrogenated to form either the unsaturated alcohol, allyl alcohol (the desired product) or the unsaturated aldehyde, propanal.
(the undesired product) (60). Thermodynamically the undesired product is favored by $\sim$35 kJ/mol so a catalyst must be used to kinetically control this reaction (61).

Previous experimental work on acrolein hydrogenation has surveyed different metal catalysts and found that silver is particularly effective (62). Extensive studies of metal identity, metal particle size, interaction of the metal with the support, reaction conditions, coverage, and alloys have been performed (60; 61; 62; 63; 64; 59; 65).

Although silver is not a traditional hydrogenation catalyst, like palladium or platinum, more active metals will result in the cleavage of C-C bonds as the double bond of acrolein is unprotected (62).

Claus and co-workers have found that the particle size strongly influences the selectivity as larger particle sizes are more selective towards allyl alcohol (65). Our own group has recently confirmed this result over a very wide range of particle sizes supported on SiO$_2$ (66). In addition, increasing the reaction pressure has also been shown to benefit the selectivity toward allyl alcohol (67) (66). It has been suggested that the low energy (111) surfaces of large Ag particles and high pressure allow for acrolein to be adsorbed in the high coverage configurations which are amenable to selective hydrogenation of the C=O bond (68).

Finally, it has been found that a great increase of selectivity towards allyl alcohol can be induced by the presence of indium in the catalyst (69). Claus reported an increase in selectivity towards allyl alcohol from approximately 40% to 60% when there is indium present as opposed to pure silver catalyst. To the knowledge of the author this catalyst is thus by far the best heterogeneous catalyst identified for this particular reaction. Presence of Ag$_3$In alloy was proven with XRD (although the peak was small in comparison to Ag) (69).
Figure 15 Selectivity of AgIn$_x$ (69).

Figure 16 shows the reaction scheme proposed by Rosch et al. involving two paths leading towards the desired product and the two other paths towards the unwanted one (62). Once adsorbed, acrolein can react with co-adsorbed hydrogen at four different locations (O, C1, C2, and C3) to produce four stable intermediates (hydroxyallyl, allyloxy, 2-formylethyl, and 1-formylethyl) (62). In this work, we will follow the example of Rosch and evaluate the selective hydrogenation of acrolein over Ag(111), Ag$_3$In(111) and AgIn$_2$(110) surfaces (shown in Figure 17) in an attempt to understand how alloying steers the selectivity. In addition, to help explain our results, XANES and density of states of the bulk structures were modeled using CASTEP.
Figure 16 Reaction scheme (62).

Figure 17 Ag(111), Ag$_3$In(111), AgIn$_2$(110).
2. SUPPORT EFFECTS IN HYDROGEN REVERSE SPILLOVER ONTO Rh₆ CLUSTERS

2.1 Introduction

The interaction of hydrogen with supported metal clusters is of crucial importance in various catalytic processes related to hydrogenation, dehydrogenation, or hydrogenolysis of petrochemicals and other organic compounds. In many of these processes, it is conceived that hydrogen spillover from the metal to the oxide support occurs whereby molecular hydrogen undergoes dissociation on the metal into atomic H, which then spills over onto the oxide support forming OH groups on the surface (70). Similarly, a process known as reverse spillover can take place when the spillover species diffuses from the surface of the support back onto the surface of the metal particle. Using density functional theory, Vayssilov et al. studied the reverse spillover of hydroxyl groups from a model zeolite structure (designed to mimic faujasite) onto a Rh₆ particle (71). Vayssilov et al. found that the reverse spillover reaction was highly exothermic (approximately −100 kJ/mol per H atom) and used their results to help explain the anomalously long but uniform Rh-Rh bond distances that were observed in EXAFS (Extended X-ray Absorption Fine Structure) measurements by the Gates group (72). Interestingly, Vayssilov et al. also found that the supported Rh clusters were effectively “oxidized” by the presence of the hydrogen as determined from Mulliken charge analysis (71). Prior to spillover, the support polarized the rhodium cluster dividing it into two Rh trimers, the
top atoms and the bottom atoms in contact with the zeolite. The atoms in contact with the zeolite have a positive charge of 0.32 e per atom whereas the top atoms of the cluster are negatively charged with -0.31 e per atom. Upon reverse hydrogen spillover, the charge distribution changes to +0.74 e for the rhodium atoms close to the zeolite, and -0.05 e for the top atoms, showing an oxidation of the Rh atoms in contact with the support and changing the overall charge of the cluster from neutral to cationic. An average Rh–Rh bond length of 2.62 Å was found for the Rh₆(3H) cluster by Vayssilov et al. in agreement with the experimental value of 2.67-2.69 Å as reported by Weber and Gates (72). Extending this work, Vayssilov and Rösch examined the reverse spillover of hydrogen onto a group of twelve metals (the 3d, 4d, and 5d metals of groups 8-11) and found that using the same M₆/zeolite Y (faujasite) model, reverse spillover was exothermic for all metals ranging from −18 kJ/mol per transferred H atom on Au₆ to −247 kJ/mol per transferred H on Os₆. In the same manner as Rh₆, all M₆ clusters were found to be cationic following reverse spillover. In that work, Vayssilov and Rösch failed to identify a key descriptor which would allow facile interpretation of the reverse spillover process.

More recently, Ivanova-Shor et al. found that using the zeolite Y model, the location of the protons was critical to the energetics of the reverse spillover process (73). For example, spillover from hydroxyl groups located in the sodalite six ring structure was actually endothermic on Au₆ (29 kJ/mol per transferred H) whereas hydrogen transfer from hydroxyl groups outside the sodalite ring was considerably more favorable (−47 kJ/mol per transferred H). Complicating this analysis is the fact that the relative stability of hydroxyl groups can change in the presence of the metal cluster.
One question that arises from the Vayssilov-Rösch collaboration is whether their results can be applied generally to other metal oxide supports. While the reverse spillover process is highly exothermic on Vayssilov and Rösch’s model for zeolite Y, it is well known that the protons on this surface are highly acidic so we can expect that proton donation to an (conjugate base) acceptor should be favorable. However, on other supports which are considerably less acidic it is not clear that this process is thermodynamically favorable. Experimental results from Gates et al. indicate that elongated Rh–Rh bonds exist for Rh clusters on a variety of supports including faujasite (72), titania (74), magnesia (75), alumina (76), and lanthana (77). The results of Vayssilov et al. indicate that the increase in the length of the Rh–Rh bonds is not solely due to the presence of hydrogen on the clusters, but also due to the formation of Rh–O bonds between the cluster and the support (71). Up to this point, only the thermodynamics of reverse spillover has been considered and kinetic issues with this system have not been examined. Therefore, to further investigate the phenomenon of reverse spillover, we extended the work of Vayssilov and Rösch to examine the interaction of Rh₆ with various (hydroxylated) supports: anatase-TiO₂(101), rutile-TiO₂(110), α-Al₂O₃ (0001), β-cristobalite SiO₂ (111), MgO (111), and LTA, a model zeolite possessing an equal number of Al and Si cations.

In order to examine reverse hydrogen spillover, we will choose models of hydroxylated surfaces which may form upon exposure to water at 1 mbar at room temperature. We have not made an exhaustive search of all possible surfaces for each oxide but we rely upon previous results from the literature to guide us in our choice of surfaces. It is important to remember, our primary goal is merely to determine if reverse hydrogen spillover is a general phenomenon so the specific choice of the surface is not critical so long as we have not chosen a surface
whose thermodynamic stability precludes its formation. We will discuss the models for the six surfaces followed by an examination of reverse hydrogen spillover over these surfaces. Finally, we have examined the kinetics of this process on the silica substrate in an effort to determine under what conditions reverse spillover will occur.

2.2 Computational Methods

The density functional theory calculations in this work are performed using the Vienna Ab Initio Simulation Package (VASP) (78) (79). A plane-wave basis set with a cutoff energy of 400 eV and ultra-soft Vanderbilt pseudopotentials (US-PP) (80) was used in all calculations reported herein. All calculations are carried out with a 2 × 2 × 1 Monkhurst Pack (81) kpoint grid except for the unit cell for zeolite-LTA (which will be discussed separately). The geometries for the individual supports are described in the Results section. The upper two layers of each surface are relaxed as well as the cluster itself in all calculations and about 12 Å of vacuum space is present between slabs. The geometries of all structures were located with the conjugate gradient method and were considered to be converged with energy within 0.001 eV and forces of less than 0.025 eV/Å. The transition states (TS) are determined by the climbing nudged elastic band (NEB) method of Henkelman and Jónsson (82) (83).

2.3 Results

The rhodium cluster used in this computational study is an octahedral Rh₆ “anti-prism” structure depicted in Figure 18. This structure was used previously in the work of Vayssilov et
al. (71), although later in Ivanova-Shor et al. (73), the authors found that a triangle prism structure was favored by 11 kJ/mol. Planar structures of Rh have been examined as well as the octahedral structure. The octahedral structure is favored over planar Rh$_6$ by 1.33 eV.

Figure 18 a) Rh$_6$ cluster with octahedral geometry used in all calculations b) Rh$_6$H$_3$ cluster.

The reverse spillover of hydrogen is represented in Figure 18(b). In the gas phase system the hydrogenation of Rh$_6$ to form Rh$_6$H$_3$ is exothermic by 1.07 eV (not that this is not the
saturation point for hydrogenation but simply a choice for our model system) and the average Rh–Rh bond length in the cluster increases from 2.56 to 2.60 Å upon adsorption of hydrogen while maintaining the octahedral structure with hydrogens adsorbing in three-fold coordinated sites on three faces of the octahedron.

Following, the initial experimental results of Weber and Gates on zeolite Y (72), Goellner et al. have shown that Rh$_6$ clusters can be assembled on P25 TiO$_2$ powder when exposing Rh(CO)$_2$(acac) to CO followed by hydrogen at 100 ºC (74). EXAFS determined that the Rh-Rh CN=4.4 (coordination number) and that Rh–Rh bond distance was 2.64 Å. The data indicate that Rh$_6$ clusters can be synthesized on TiO$_2$ and that the long Rh–Rh bond distances on zeolite Y are also evident on TiO$_2$. Therefore, we begin our examination of support effects with both rutile and anatase surfaces.

The rutile (110) surface (hereafter designated r-TiO$_2$(110)) is among the most studied surfaces in catalysis (84). Hydroxyl groups in bridging oxygen locations have been observed by STM as a consequence of background water adsorbing and dissociating across oxygen vacancies in the bridging row (85). We have followed the example of Selloni et al. (86) and created a hydroxylated r-TiO$_2$(110) surface by hydrogenation of 50% of the bridging oxygens of the surface. A 2 × 2 unit cell, 11.8 × 13.0 Å, with four stoichiometric layers of TiO$_2$ (approximately 12 Å thick) with 12 Å of vacuum between slabs was used shown in Figure 19. The positioning of the Rh$_6$ cluster was done so the cluster sits between rows of bridging oxygens and bonds to the surface with an adsorption energy of −3.34 eV through Rh–O bonds formed between the lower triangle of the Rh$_6$ cluster and surface oxygen as shown in Figure 20. Two Rh atoms bond to
both bridging oxygen (with a bond length of 2.15 Å) and 3-fold coordinated surface oxygen (with a bond length of 2.18 Å) whereas the third Rh atom bonds only to 3-fold coordinated oxygens with two Rh–O bonds of 2.32 Å. The Rh-Rh bond distances on the supported cluster average 2.54 Å indicating that the support does not induce large changes in the bond distance due to lattice matching or any other effect. On the hydroxylated r-TiO₂(110) surface, the reverse spillover of hydrogen from the hydroxyl groups to the Rh₆ cluster is only weakly exothermic with a ΔE= –0.37 eV. This stands in stark contrast to the previous work of Vayssilov et al. on zeolite Y (71) indicating that the identity of the support is indeed important to the reverse spillover process. Upon reverse spillover the cluster deforms slightly with the Rh-Rh bonds distances increasing to 2.58 Å as expected with the hydrogen atoms bridging between Rh atoms of the lower triangle and the upper triangle (the structure is shown in Figure 20b). In addition, the Rh-O bonds contract (the Rh-O bonds to bridging O are now 2.07 Å; the other Rh-O bonds average 2.18 Å). As noted previously, some charge transfer occurs upon reverse spillover. Prior to the reverse spillover event, the Rh₆ cluster was slightly cationic as the atoms in contact with the support possessed a small positive charge of +0.23 e- per atom whereas the atoms not in contact with the support were neutral for an overall average charge of +0.12 e-. However, just as in the case of Vayssilov et al. (71) reverse spillover results in charge transfer from the cluster to the support and the average charge on each atom decreases by 0.12 e-, resulting in a new average charge of +0.24 e-.
Figure 19 Side view of r–TiO$_2$(110). White atoms are Hydrogen, red atoms are Oxygen, and grey atoms are Titanium. Red lines indicate the unit cell boundaries.

Figure 20 Structure of Rh$_6$ cluster supported on r-TiO$_2$(110) a) before and b) after reverse spillover. White atoms are Hydrogen, red atoms are Oxygen, grey atoms are Titanium and blue atoms are Rhodium.
However, since the experiments of Goellner and Gates involving TiO$_2$ were performed using P25 as a support, it is prudent to examine both rutile and anatase surfaces. For the Anatase (101) surface shown in Figure 21, hereafter designated a-TiO$_2$(101)) a 2 × 2 unit cell, $15.2 \times 10.3$ Å, ~10 Å thick, (3 stoichiometric layers) with ~13 Å of vacuum space between slabs was used. Hydroxylated surfaces of anatase could be created in two ways. First, a surface was created by addition of hydrogen to oxygens from the a-TiO$_2$(101). This surface is somewhat analogous to the hydroxylated r-TiO$_2$(110) surface. A second hydroxylated anatase surface was created by adding water molecules to the bridging oxygens as done by Hamraoui et al. (87) shown in Figure 22.
According to Hamraoui, the hydrogens of the water molecule adsorbed on the anatase (101) surface form weak hydrogen bonds with the surface oxygens 2.06 Å in length and the Ti adsorption site becomes a 6-fold coordinated geometry forming bonds with the oxygen of the adsorbed water. The surface is saturated with eight water molecules, which is the most stable state at $P_{H_2O} = 0.01$ atm and 300 K. The model presented in this work has 4 water molecules adsorbed on the surface (to mimic slightly elevated temperature/lower partial pressure conditions) with average adsorption energy of 0.77 eV. The cluster was placed to form two Rh–O bonds of $2.04 \pm 0.01$ Å on the surface as well as two Rh–O bonds of 2.27 Å between the third Rh of the bottom triangle and the O from a water molecule as shown in Figure 23a. The Rh$_6$ cluster bonds with an adsorption energy of $\sim 2.79$ eV. Just as in the case of Rh$_6$ bonding to
r-TiO$_2$(110), the Rh-Rh bond length changes only slightly (to 2.53 Å) in response to the presence of the underlying substrate. Reverse spillover of three hydrogens onto the cluster was carried out leaving three OH groups bonded to the surface which results in the creation of two additional Rh-O bonds (and a lengthening of the bond between Rh and O from the single remaining intact water molecule as shown in Figure 23b.

Figure 23 Structure of Rh$_6$ cluster supported on α-TiO$_2$(101) a) before and b) after reverse spillover using a structure with H attached to surface oxygens. White atoms are Hydrogen, red atoms are Oxygen, and grey atoms are Titanium.
The reverse spillover event is exothermic with a reaction enthalpy $\Delta E = -0.90$ eV. In addition, we have compared these results using water as the source of H spillover to a system which has terminal hydroxyl groups in a similar fashion to our model for hydroxylated r-TiO$_2$(110) in which hydrogen adds to surface oxygens presumably by the dissociation of water across oxygen defects. When using this model for hydroxylated a-TiO$_2$(101), the adsorption energy ($E_{\text{ads}} = -3.33$ eV) and cluster geometry (avg. Rh-Rh bond is 2.52 Å) are not significantly different those of the Rh$_6$ cluster adsorbed on the surface suggested by Hamraoui et al. However, the reverse spillover reaction (depicted in Figure 24) is now somewhat more exothermic with a reaction enthalpy $-1.74$ eV (and clearly more exothermic than on r-TiO$_2$). Our initial results on TiO$_2$ suggest that spillover is highly sensitive to the nature of the support and that the creation of defects will strongly influence the thermodynamics of hydroxyl group formation and stability on the substrate.
Based upon these results for TiO₂, a number of other substrates were examined in an effort to understand if there are general trends that may be elucidated with regard to support effects in these systems. Al₂O₃, SiO₂ and MgO are among the most common catalytic supports, therefore, we chose to examine a model for each of these surfaces. Beginning with Al₂O₃, the α-Al₂O₃ (0001) with a 2 × 2 unit cell shown in Figure 25, 8.3 × 9.6 Å, with four repeating stoichiometric tri-layers (Al-3O-AL) ~8 Å thick and ~12 Å of vacuum between slabs. The O-terminated surface was fully hydrogenated with hydrogens bonded to each surface oxygen on both sides of the slab (this quenches any polarity through the slab). There exists a wealth of
experimental evidence that indicate that hydroxyl groups exist on the α-Al₂O₃(0001) surface under relatively mild conditions (88; 89; 90; 91). In fact, full hydroxylation of the (0001) face of alumina has been shown to be thermodynamically favorable in water vapor pressures as low as 1 torr (92; 93; 94).

Figure 25 Side view of α-Al₂O₃(0001). White atoms are Hydrogen, red atoms are Oxygen, and magenta atoms are Aluminum. Red lines indicate the unit cell boundaries.
The Rh₆ cluster was placed on the surface to form 3 Rh–O bonds of 2.28 Å shown in Figure 26a. The cluster is bound to the surface with adsorption energy of -0.89 eV, significantly weaker than on the TiO₂ surfaces. The surface hydrogen bonded to each oxygen was then allowed to be spilled over onto the cluster with a reaction enthalpy of -0.04 eV. The Rh-O bonds contract dramatically to 1.92 Å upon reverse spillover while the average Rh-Rh bond distance increases slightly from 2.51 Å to 2.56 Å as depicted in Figure 26b. Freund and co-workers have shown surface OH groups on a hydroxylated alumina thin film are removed upon evaporative deposition of rhodium (95). XPS (X-ray Photoelectron Spectroscopy) spectra of the rhodium particles (Rh 3d) showed an approximately 0.5 eV shift to higher binding energies as compared to similar sized rhodium particles support on a Al₂O₃ thin film which does not possess hydroxyl groups, providing evidence that the presence of the hydroxyl groups on the film directly affects electronic structure of the rhodium particles (96). Our calculations indicate that a positive charge of 0.30 e- per Rh is present after reverse spillover which would be consistent with the higher binding energy observed in Freund’s XPS experiments. One could conclude that the disappearance of the hydroxyl groups and the shift to higher binding energies are both related to a reverse spillover process.
Figure 26 Structure of Rh$_6$ cluster supported on $\alpha$-Al$_2$O$_3$ (0001) a) before and b) after reverse spillover. White atoms are Hydrogen, red atoms are Oxygen, magenta atoms are Aluminum and blue atoms are Rhodium.

MgO has a rock salt structure and its (111) surface will either be oxygen terminated or magnesium terminated. As we wished to focus upon the presence of hydroxyl groups and their role in reverse spillover, we began with the oxygen terminated MgO (111) surface and added hydrogen to each oxygen for charge compensation. Furthermore, the MgO(111) slab was constructed as a mirror surface to achieve an 11 layer structure shown in Figure 27. The dimensions of the unit cell used are 10.3 $\times$ 11.9 Å, ~ 13 Å thick with 16 Å of vacuum. The Rh$_6$ cluster was placed above OH groups on the surface in similar way as on the $\alpha$-Al$_2$O$_3$(0001) surface as shown in Figure 28a, so as to maximize the potential for Rh–O bond formation (two
Rh-O bonds of 2.30 Å and one Rh-O bond of 2.17 Å form). Similar to α-Al₂O₃(0001), Rh₆ bonds weakly to the MgO(111) surface with an adsorption energy of −1.23 eV. We did not examine the stoichiometric MgO(100) surface since previous researchers have observed that water cannot dissociate across this surface to create surface hydroxyl groups (97; 98; 99). In fact, in a limited number of calculations with a hydroxylated MgO(100) surface, we found water to spontaneously reform. As in the case of r-TiO₂(110) and α-Al₂O₃(0001), the reverse spillover event is only mildly exothermic (−0.75 eV). After reverse spillover (and therefore removal of H from the oxygen atoms in contact with the Rh₆ cluster), the Rh-O bonds dramatically contract to an average distance of 1.90 Å (shown in Figure 28b). Bader charge analysis for the MgO supported Rh₆ cluster reveals similar behavior to the Al₂O₃ supported cluster as the cluster goes from charge neutral to +0.28 e⁻.
Figure 27 Side view of MgO(111). White atoms are Hydrogen, red atoms are Oxygen, and light green atoms are Magnesium. Red lines indicate the unit cell boundaries.

Figure 28 Structure of Rh₆ cluster supported on MgO(111) a) before and b) after reverse spillover. White atoms are Hydrogen, red atoms are Oxygen, light green atoms are Magnesium and blue atoms are Rhodium.
Like titania, silica possess multiple crystal structures (quartz, cristobalite, and stishovite). However, unlike titania, high surface area supports are often amorphous not crystalline. We chose the SiO$_2$ β-Cristobalite (111) surface as a model surface for SiO$_2$ based upon previous work by Janik and coworkers (100). A 2 × 2 unit cell, 9.1 × 10.5 (4 stoichiometric layers with a thickness of ~15 Å) model for the SiO$_2$(111) surface was constructed as shown in Figure 29. The hydroxylated surface was created by adding OH groups to the surface per the model of Wang et al. (101) whereby only isolated silanols are created (as opposed to geminal silanols) which are separated by ~ 5 Å. The Rh$_6$ cluster was placed on the surface (shown in Figure 30a) such that three Rh-O bonds of 2.31 Å are created with an adsorption energy of −0.84 eV. The reverse spillover event is a bit more exothermic (−1.32 eV) than on Al$_2$O$_3$ or MgO, but the resulting charge transfer of +0.32 e- was found to be fairly similar. After reverse spillover, the Rh$_6$ cluster forms three Rh-O bonds with the surface of 1.94 Å apiece as depicted in Figure 30b, showing very similar behavior to MgO and Al$_2$O$_3$. 
Figure 29 Side view of $\beta$–$\text{SiO}_2(111)$. White atoms are Hydrogen, red atoms are Oxygen, and gold atoms are Silicon. Red lines indicate the unit cell boundaries.

Figure 30 Structure of $\text{Rh}_6$ cluster supported on $\beta$–$\text{SiO}_2(111)$ a) before and b) after reverse spillover. White atoms are Hydrogen, red atoms are Oxygen, gold atoms are Silicon and blue atoms are Rhodium.
We conclude our study with a zeolite, LTA (linear type A), which has a 1:1 ratio of alumina to silica to compare our results directly with those of Vayssilov et al. (71). LTA has three dimensional unit cell of 24.6 Å with cavities of 14.9 Å in diameter and openings with a diameter of 5.6 Å. Since the unit cell of LTA comprises 576 atoms (96 Si, 96 Al and 384 O) (102), calculations involving the entire unit cell are impractical using density functional theory. Therefore, in order to lower the computational burden, we created a small unit cell of LTA which is 1/8 the size of the true LTA unit cell (a single cavity is contained in a cubic cell 12.3 Å per side with 12 Si, 12 Al, and 48 O) shown in Figure 31. This requires the creation of 48 Si–O–Si linkages and Al–O–Al linkages to replace 48 of the 384 Al–O–Si linkages in the true unit cell of LTA (a 2×2×2 supercell of our smaller model) which then implies our cell has 6 Si–O–Si linkages, 6 Al–O–Al linkages and 36 Al–O–Si linkages). To stabilize the negative charge created by the substitution of alumina into the silica, 12 hydrogen atoms were placed on the inner cavity of the LTA. When the Rh₆ cluster was placed in the LTA cavity, two of the Rh atoms (unlike every other case in which three Rh atoms contact the substrate) are in contact with the substrate due to the curvature of the pore with each Rh atom possessing 2 Rh-O atoms of 2.16 ± 0.08 Å and the adsorption enthalpy is –1.56 eV (shown in Figure 32a). In a similar fashion to SiO₂ and Al₂O₃, the cluster has only a very small positive charge (+0.02 e-/ per Rh atom). The reverse spillover on the Rh₆ cluster on LTA is highly exothermic with a reaction enthalpy of –3.74 eV (shown in Figure 32b). As in the case of SiO₂, the bader charge analysis revealed that the cluster loses an average of 0.34 e- after reverse spillover so that the cluster has an overall charge +0.36 e- per atom. Upon reverse spillover, a third Rh-O bond is formed each with a bond distance of 2.15 ± 0.01 Å.
Figure 31 Structure of zeolite LTA. White atoms are Hydrogen, red atoms are Oxygen, gold atoms are Silicon and magenta atoms are Aluminum. Red lines indicate the unit cell boundaries.

Figure 32 Structure of Rh$_6$ cluster supported on zeolite LTA a) before and b) after reverse spillover. White atoms are Hydrogen, red atoms are Oxygen, gold atoms are Silicon, magenta atoms are Aluminum and blue atoms are Rhodium.
2.4 Discussion

Clearly from the results, the different supports show dramatically different behavior for reverse spillover of hydrogen from the support to the Rh$_6$ cluster. Before we discuss the differences in reverse spillover, a few commonalities should be recognized. All surfaces studied presented an exothermicity for the Rh$_6$ hydrogen spillover reaction except Al$_2$O$_3$, which is thermoneutral. In addition, on all surfaces, Rh-Rh bonds expanded upon reverse spillover with the Rh$_6$ cluster on LTA having the largest average bond expansion (0.09 Å) and Rh$_6$ on rutile had the least bond expansion with a difference of 0.04 Å. In all cases the Rh-Rh bond expansion was accompanied by a Rh-O contraction (and in some cases an increase in the number of Rh-O bonds) upon reverse spillover. The bader charge analysis performed on each surface shows a cationic effect on the cluster after the spillover, which agrees with the results observed by Vayssilov et al. showing the cluster undergoes an oxidation after the reaction is carried out.

Despite the universal aspects of reverse hydrogen spillover mentioned above, the exothermicity and therefore the thermodynamics (and by extension the kinetics) of reverse spillover varies substantially across the range of supports considered. Just as the amount of hydrogen that could be predicted to be spilled over to a given metal cluster has been found to be dependent on the identity of the metal, we find here that for a given metal cluster the amount of hydrogen that will adsorb on the cluster is dependent on the identity of the support. For example, the energy minimum for reverse spillover on Al$_2$O$_3$ for our system is found when just two hydrogen atoms are attached to the Rh$_6$ cluster, when the third hydrogen atom spills over from the support, the energy of the system increases by 0.65 eV. In this work we did not
establish the favorable number if hydrogen atoms that could be transferred for each surface, we arbitrarily chose 3 hydrogens as a basis so as to make an easy comparison with the earlier work of Vayssilov et al. In addition, we did not explore the effect of cell size on the calculation. Presumably the larger the cell size, the more favorable reverse spillover will become. We seek to elucidate trends in the process in order to identify a simple descriptor of the process to rapidly identify systems for which reverse spillover is important. Possible variables include the amount of charge transfer involved, the binding of Rh₆ to the substrate and the strength of O-H bonds on the support. In Table I the bader charge for Rh₆ before and after reverse spillover on each of the supports is presented along with the enthalpy of reaction for the reverse spillover process. Naively one could suggest that the more charge transfer is involved, the greater the driving force for reverse spillover and hence the more exothermic the reverse spillover process should be. However, the bader charge difference between the initial state and final state does not appear to be an accurate descriptor for predicting how exothermic the reverse spillover process will be. For example, all of the samples except r-TiO₂ had a donation of about 0.30 e- to the support upon reverse spillover. Despite this similarity, the reverse spillover on α-Al₂O₃ and LTA have very different reaction enthalpies: on alumina the reaction is thermoneutral but on LTA the reaction is highly exothermic. Similarly the absolute magnitude of the positive charge on the Rh₆H₃ cluster does not correlate with reaction enthalpy either.
Table I Comparison of Charge Transfer

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<th>r-TiO₂</th>
<th>a-TiO₂</th>
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<th>Al₂O₃</th>
<th>SiO₂</th>
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<td>-0.02</td>
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</tr>
<tr>
<td>Rh₆H₃</td>
<td>0.24</td>
<td>0.17</td>
<td>0.28</td>
<td>0.30</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>ΔE (eV)</td>
<td>-0.37</td>
<td>-1.74</td>
<td>-0.75</td>
<td>-0.04</td>
<td>-1.14</td>
<td>-3.74</td>
</tr>
</tbody>
</table>

Another logical predictor for the probability for reverse spillover would be the O-H bond strength of the support hydroxyl group. One could hypothesize that a strong OH bond strength results in poor hydrogen spillover from the surface onto the cluster. It would be expected that the surfaces with more favorable thermodynamics for reverse spillover would be the supports with weaker OH bond strengths. Indeed, strong O-H bonds are found for MgO and Al₂O₃ surfaces and reverse spillover is nearly thermoneutral. However, the hydroxyl group O-H bond strength is even weaker on r-TiO₂, but the reaction is also nearly thermoneutral. In addition, the reaction is most exothermic on LTA but its OH bond strength is also stronger than those on r-TiO₂.

One explanation is that the O-H bond strength may change when the Rh₆ cluster is present. Ivanova-Shor et al. found that the acidity of different support protons (or the O-H bond strength) changed dramatically when the metal cluster was adsorbed on the support. For example, on the bare zeolite Y model support, O4H groups were determined to be less acidic
than O1H groups; the deprotonation energy of O1H groups was evaluated at 25 kJ/mol lower. In contrast, adsorption of bare Ir₆ cluster reversed the strength of the acidity of OH groups in the vicinity of the adsorbed metal clusters: the deprotonation energy of O1H groups was calculated to be 51 kJ/mol larger than for O4H groups. The degree to which the O-H bond strength may be perturbed could potentially be related to the binding strength of the Rh₆ cluster to the support. In addition, the strength of the interaction between the metal cluster and the support may affect the thermodynamics of reverse spillover. It stands to reason that supports which do not bind the cluster strongly may be relatively inert and that reverse spillover should be less favorable in these cases. Looking at the PDOS of Rh₆/r-TiO₂ vs. Rh₆/SiO₂ as depicted in Figure 33, one can see that the d-band center of the cluster shifts away from the Fermi level when the cluster is in contact with a support that interacts strongly with the cluster as the d-band center moves from -1.23 to -1.83 eV. Therefore, the when Rh₆ is bound to r-TiO₂ we expect that the Rh-H bonds formed will be weaker and the reaction enthalpy for reverse spillover will decrease relative to Rh₆/SiO₂. We can easily illustrate the weakening of adsorbate bonds by examining CO adsorption over Rh₆/SiO₂ and Rh₆/r-TiO₂. In both cases, CO is adsorbed atop to a Rh atom which is not in contact with the support.

Table II shows the adsorption energy for the Rh₆ cluster on all the surfaces studied. However, contrary to our hypothesis, when examining the data for the Rh₆ adsorption energy vs. reaction enthalpy, no clear trend emerges. Adsorption of Rh₆ to LTA has a moderate binding energy along the scale of the various supports, yet the reverse spillover event was the most exothermic. The cluster was strongly adsorbed onto both TiO₂ surfaces regardless of the great difference between the ∆E of rutile and anatase. The cluster was absorbed weakly onto Al₂O₃.
surface which is also the least exothermic reaction surface, negating any trend. One could extend this further by attempting to combine the factors that we outline above. Since the exothermicity should decrease with the adsorption energy and decrease with increasing O-H bond strength, we examined how the reaction enthalpy correlates with the sum of these parameters. However, we find that summing these parameters gives a strikingly similar value for all support surfaces, again indicating that this does not capture the all the relevant interactions and that these systems are complex enough to defy analysis by a simple descriptor. Previously Rösch and Vayssilov examined energetics of the adsorption of $M_6$ compared to the exothermicity of reverse spillover of hydrogen onto these clusters and also found no general trend. Therefore, our lack of a definitive trend across supports is not surprising.

Table II OH Bond Strength vs. Reaction Enthalpy. The OH bond strength is referenced to H2 in the gas phase.

<table>
<thead>
<tr>
<th></th>
<th>r-TiO$_2$</th>
<th>a-TiO$_2$</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>LTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{OH}$ (eV)</td>
<td>-1.53</td>
<td>0.09</td>
<td>-3.36</td>
<td>-2.58</td>
<td>-3.40</td>
<td>-2.22</td>
</tr>
<tr>
<td>$\Delta E$ (eV)</td>
<td>-0.37</td>
<td>-1.74</td>
<td>-0.75</td>
<td>-0.04</td>
<td>-1.32</td>
<td>-3.74</td>
</tr>
</tbody>
</table>
Table III Rh\textsubscript{6} Adsorption Energy

<table>
<thead>
<tr>
<th></th>
<th>r-TiO\textsubscript{2}</th>
<th>a-TiO\textsubscript{2}</th>
<th>MgO</th>
<th>Al\textsubscript{2}O\textsubscript{3}</th>
<th>SiO\textsubscript{2}</th>
<th>LTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>E\textsubscript{ads} (eV)</td>
<td>-3.38</td>
<td>-3.33</td>
<td>-1.06</td>
<td>-0.89</td>
<td>-0.66</td>
<td>-1.56</td>
</tr>
<tr>
<td>ΔE (eV)</td>
<td>-0.37</td>
<td>-1.74</td>
<td>-0.75</td>
<td>-0.04</td>
<td>-1.14</td>
<td>-3.74</td>
</tr>
</tbody>
</table>

Figure 33 Comparison of the PDOS of a Rh\textsubscript{6} cluster supported on TiO\textsubscript{2}(110) and β-SiO\textsubscript{2}(111).
Although the reactions studied so far are thermodynamically favorable, this does not indicate that the reaction will occur, therefore the kinetics of reverse spillover need to be studied.

Figure 34 depicts the migration of a random proton from the SiO\textsubscript{2} surface onto the Rh\textsubscript{6} cluster. The first hydrogenation step has an enthalpy of \(-0.66\) eV (each ensuing step is less and less exothermic). The activation barrier for this initial hydrogenation is 0.66 eV. Recently Yacobsen and co-workers recently calculated the reverse spillover of hydrogen from graphene onto Pd\textsubscript{4} clusters and found that the barrier is 0.83 eV with a reaction enthalpy of 0.15 (i.e. in this its endothermic due to the large amount of hydrogen on the Pd\textsubscript{4} cluster) (103). Although both the metal and support are different, it is interesting to note how similar the barriers are. This implies that barrier is easily surmountable at typical hydrogenation reaction temperatures and therefore should be observed in all of these types of systems.
2.5 Conclusions

The reverse spillover does depend greatly on the identity of the support. To identify the major factors affecting the energy of hydrogen transfer from OH groups to a metal cluster, we tried to correlate the thermodynamics of reverse hydrogen spillover with various simple key characteristics: (i) degree of charge transfer, (ii) strength of O-H bond of the support (iii) the adsorption energy of the Rh₆ cluster on the support. However, we did not find any substantial correlation. This failure is likely due to the complex nature of the process. The interaction in
question is influenced not only by O-H bond strength and the adsorption energy of the Rh$_6$ cluster. Initial calculations show that the reverse hydrogen spillover barriers are less than 0.70 eV, therefore this phenomenon could occur in typical reaction conditions for hydrogenation reactions over Rh catalysts.
3. STUDY OF d-band TRANSITION METAL ALLOYS: PdX (X = Co, Ni, Cu, Rh, Ag, Ir, Pt, Au, Zn, Ga, Ge) XANES AND DENSITY OF STATES.

3.1 Introduction

The possibility to tune the catalyst performance and improve its desired properties relies on developing a detailed understanding of how the catalyst functions. To this end, the fundamental properties of d-band transition metals have been studied by Norskov and coworkers using Density Functional Theory (3). Norskov and Hammer proposed that chemisorption of simple adsorbates like CO can be understood using a simple model describing the electronic states of the adsorbate and the d-band valence of the transition metal. Their work demonstrated that a trend in the adsorption behavior could be developed relating the strength of adsorption to the energy of the d-band center with respect to the Fermi level. Since the sp bands of d-band transition metals are relatively similar, the position of the d-band center with respect to the Fermi level is the critical factor which determines the strength of the interaction of the metal with the adsorbate. In relation to the Fermi level, a downshift in the d-band center of the metal implies a more stable structure, thus, less reactive. An opposite effect occurs when the d-band center shifts up towards the Fermi level resulting in a more reactive metal.
Positioning of the $d$-band center has been shown to be sensitive to electronic changes as well as geometric effects. Hammer et al. have demonstrated that coordination number has a direct effect on the $d$-band center location with respect to the Fermi level (4). Overcoordination results in increased $d$-band overlap resulting in a low reactivity of the structure, and accordingly, an undercoordination of atoms results in a less crowded $d$-band, increasing reactivity. This can be explained by rectangular $d$-band model, where the overall width of the $d$-band either contracts or expands to maintain constant electron filling of the band.

Expansion of the $d$-band following the rectangular model will cause the center of the $d$-band to shift away from the Fermi, a contrary effect will happen when the $d$-band undergoes contraction, where a compensation effect will shift the center towards the Fermi.

The Hammer and Norskov $d$-band model has been applied to other adsorbates. Greeley and Norskov applied the model to oxygen binding on binary transition metal surface alloys using DFT, concluding that adsorption of oxygen can also be described by a single parameter of the $d$-band center (6). Numerous examples have now been illustrated by the Norskov group and others whereby $d$-band theory has been used to predict catalytic performance for many reactions (3; 4; 6; 104). For example, Norskov et al. have used the $d$-band center to predict the oxygen adsorption energy on Pt$_3$M alloys (M= Ti, Co, Fe, Ni) (105), and have correlated it to the oxygen reduction reaction for polymer electrolyte membrane fuel cells.

In order to understand alloy properties, one would like to understand the origin of the $d$-band center shifts in alloys. Alloying alters the structure and composition of a catalyst usually giving it intermediate properties between those of the pure components. Roudgar and Gross
used DFT to examine hydrogen adsorption on Pd(111), Cu(111), as well as overlayers of Pd on Cu(111) and Cu on Pd(111) and expansion/contraction of one metal to the other’s lattice (106). Hydrogen adsorption on this alloy has an intermediate energy lying between those of the pure constituents increasing in strength from -0.05 eV on Cu(111) to -0.1 eV on a Pd monolayer on Cu(111), and finally to -0.4 eV on Pd(111). Another example of intermediate behavior of alloys is the dissociative adsorption of H$_2$ (107). Kitchin et al. modeled dissociation of H$_2$ on different metal alloys including NiPt$_3$, for which the dissociative adsorption energy of H$_2$ has a value (-0.52 eV) in between those of the pure components (-0.43 eV for Pt(111) and -0.65 eV for Ni(111)). However, alloys may also possess unique properties leading to behavior that falls outside of the range between the pure components (13). For example, selective oxidation of saturated hydrocarbons to produce cyclohexanol, in which the catalyst with best selectivity (Pd, 99.9%) has a very low yield (<3%) and on the other hand, a less selective catalyst (Au, 81.8%) has a higher yield (16.2%). The PdAu alloy has a synergistic effect on the yield of cyclohexanol with an increase to 26.8% (108).

While the $d$-band center model seems to work very well for a wide range of alloys, there are exceptions. Xin and Linic have recently demonstrated that for Pt and Pd skin alloys where Pd and Pt are placed above 3d metals, the trend in the adsorption energy with $d$-band center energy is inverted for highly electronegative adsorbates like OH (7).

In the case study of OH adsorption on skin alloys, interaction between the $sp$-band of the support governs the strength and length of the bond. On the other hand, orthogonalization between the renormalized adsorbate state and the metal $d$-state results in repulsion. Electron
transfer between the subsurface metal and the surface skin of Pd or Pt depends on the electronegativity of the metal in the sublayer. The alloys with subsurface metals on the left side of the periodic table, which are less electronegative, will have increased electron transfer to the surface and thus greater stabilization of the $d$-band. In addition, as the alloying metal moves to the left, the adsorbate bond length increases in order to achieve optimal electron density. The longer the bond distance the stronger the bond formed as the amount of Pauli repulsion decreases with increasing bond length. This behavior described by Xin and Linic is unique to systems with nearly fully occupied $d$-band and with adsorbates with almost completely filled valence shells (for example, the adsorption of O which is less electron rich than the O atom of OH, follows typical $d$-band model behavior).

Although we are beginning to understand late $d$-band transition metal bimetallic catalysts, there is still considerable progress to be made. Even less is understood about alloy catalysts where late $d$-band transition metals are alloyed with metals lying outside that regime. For example, PtSn, a popular catalytic reforming catalyst, involves the presence of a metal whose $d$-band is fully filled and whose valence electrons are $p$-electrons. Trends in the behavior of alloys which involve $d$-band transition metals and $p$-electron metals have not yet received substantial examination.

A systematic evaluation of these systems, bringing together experimental and theoretical input is critical to produce a new generation of catalyst with tunable properties and greater selectivity and improved resistance to deactivation.
Among the few experimental probes of electronic structure of solids is X-ray adsorption spectroscopy (XAS). X-ray absorption spectroscopy can be divided into two parts: X-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) (109). The variation in the XANES intensity gives information about the empty valence orbitals into which an ejected core photoelectron can scatter. The XANES portion of the XAS can be simulated by examination of the oscillator strength defined by the overlap integral between the core state and the valence state. Comparison between the trends of the simulated XANES and the calculated PDOS will give us insight into the electronic structure of alloys and the perturbation to the hybridization of the $d$-orbitals due to alloying with various transition metals as well as with main metals.

3.2 Methodology

Density functional theory calculations were carried out using the Vienna Ab Initio Simulation Package (VASP) (37) (38) (39). A plane-wave basis set with a cutoff energy of 400 eV and projected augmented wave pseudopotentials (47) (48) were used in all calculations. The Perdew-Burke-Ernzerhof (PBE-GGA) form of the correlation and exchange energy was used in all calculations (51) (52). All calculations are carried out with a 9 x 9 x 9 Monkhurst Pack kpoint grid, except Ga (9x7x9), Zn and Co (9x9x7). Bulk structures of single metals were optimized using as a starting point the available library structures of Material Studio 5.5 software by Accelrys, with exception of Ga in which case a $\gamma$-galium structure was constructed (110). Bimetallic alloys were constructed by a 1:1 Pd replacement with the atom of interest. An exception to the bimetallic construction is PdCu in which case an existing phase was used by
using the LaB₆ cubic, space group Pm3m, prototype (110). All structures were optimized by allowing ion relaxation followed by a cell volume optimization; these cycles were repeated finishing with the ion relaxation step.

In order to look at electronic interactions between atoms, CASTEP DFT code was used, in particular the modules for EELS and DOS within it. CASTEP possesses a module which allows for simulation of an EELS (XANES) spectra based on overlap integral of the core state and the final state (55). The core state is evaluated using an all electron calculation of an isolated atom, whereas the pseudowavefunction for the final state is generated by an ultrasoft pseudopotential calculation within CASTEP. Gaussian broadening of 0.2 eV was applied to mimic the instrument broadening and the effect of smearing due to the finite lifetimes of the final states and the fact that calculations necessarily involve a finite number of k-points.

Due to the additive nature of the density of states, a normalized per atom density is plotted and reported herein.

3.3 Results

Before an examination of the electronic and geometric effects in the alloys can be undertaken, the effects of changes in M-M bond distances must be understood since the equilibrium bond distances of several of the alloys varies significantly as compared to their pure monometallic bulk distances. Therefore calculations were performed for a model Pd(111) slab whereby the lattice was expanded and contracted by 5% in the x and y directions. Figure 35 shows the effect of this lattice contraction and expansion on the PDOS and corresponding
simulated XANES. Compression of the surface lattice led to an increase in the XANES edge. Expansion of the lattice has a decrease in the leading edge as a result. Changes in the XANES have been related to the unoccupied states and thus the Density of States profile is able to reflect the XANES change for the density near the Fermi edge. It is clear that the expansion of Pd(111) has shifted the center of the $d$-band towards the Fermi edge from -1.64 eV to -1.38 eV. A simple way of explaining this behavior through $d$-band theory would be due to the lack of overlapping of the $d$ orbitals, Pd in expansion would then feel underbonded and thus would become more reactive. In contrast, as the weighted $d$-band center shifts away from the Fermi level, the surface is more stable thus less reactive, a similar explanation can be given for the Pd(111) in compression, in which the Pd atoms are so close to each other that the $d$-$d$ orbital hybridization is increased resulting in an ‘overbonded’ Pd and thus shifting away from the Fermi edge to -2.03 eV. Keeping in mind these two effects of the geometry and hybridization on the XANES and the DOS we will analyze the alloys of Pd-X.
A series of PdX alloys were simulated where X is a transition metal (Co, Ni, Cu, Rh, Ag, Ir, Pt and Au). Additionally, effect of other metals, different from the transition metals, has been studied with alloys composed of Pd with Zn, Ga, and Ge. Figure 56 (Introduction, Chapter 1) shows the elements of the transition metal group that will be presented in this work.

Experimental XANES of PdPt alloy supported on SiO₂ for both, the Pd and the Pt edge, are shown in Figure 36.
Figure 36 Top: experimental XANES of Pt and PdPt (Pt edge). Bottom: experimental XANES of Pd and PdPt (Pd edge).
Bond distances of pure metals and of the bimetallics are given in Tables IV and V respectively. Bond lengths of the bimetallics are measured from the Pd atom to the nearest X metal atom as well as from X to X closest neighbor distances. The distances reported herein are not experimental bulk distances but simulated distances after optimization of the model with VASP. We will discuss each of the alloys according to their grouping in the periodic table and attempt to elucidate any trends which may be present.

Table IV Pure element bond distances.

<table>
<thead>
<tr>
<th>Element</th>
<th>Bond distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>2.44</td>
</tr>
<tr>
<td>Ni</td>
<td>2.48</td>
</tr>
<tr>
<td>Cu</td>
<td>2.57</td>
</tr>
<tr>
<td>Rh</td>
<td>2.72</td>
</tr>
<tr>
<td>Pd</td>
<td>2.79</td>
</tr>
<tr>
<td>Ag</td>
<td>2.94</td>
</tr>
<tr>
<td>Ir</td>
<td>2.74</td>
</tr>
<tr>
<td>Pt</td>
<td>2.82</td>
</tr>
<tr>
<td>Au</td>
<td>2.95</td>
</tr>
</tbody>
</table>
Table V Bimetallic bond distances

<table>
<thead>
<tr>
<th>Pd-X alloy</th>
<th>Pd-X Bond Distance (Å)</th>
<th>Pd-Pd Bimetallic Bond Distance (Å)</th>
<th>X-X Bimetallic Bond Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdCo</td>
<td>2.64</td>
<td>2.64</td>
<td>2.64</td>
</tr>
<tr>
<td>PdNi</td>
<td>2.63</td>
<td>2.71</td>
<td>2.71</td>
</tr>
<tr>
<td>PdCu</td>
<td>2.62</td>
<td>3.02</td>
<td>3.02</td>
</tr>
<tr>
<td>PdRh</td>
<td>2.75</td>
<td>2.75</td>
<td>2.75</td>
</tr>
<tr>
<td>PdAg</td>
<td>2.86</td>
<td>2.86</td>
<td>2.86</td>
</tr>
<tr>
<td>PdIr</td>
<td>2.76</td>
<td>2.76</td>
<td>2.76</td>
</tr>
<tr>
<td>PdPt</td>
<td>2.80</td>
<td>2.80</td>
<td>2.80</td>
</tr>
<tr>
<td>PdAu</td>
<td>2.87</td>
<td>2.87</td>
<td>2.87</td>
</tr>
</tbody>
</table>

Tables VI and VII contain the weighted $d$-band center for the pure metal and the bimetallic respectively. The $d$-band center for the bimetallic is reported for both edges, Pd and the X metal. Weighted $d$-band centers are estimated by including all states, filled and empty, of the partial density of states profile obtained using CASTEP.
Table VI Weighted $d$-band centers for pure elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>$d$-band center (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>-1.53</td>
</tr>
<tr>
<td>Ni</td>
<td>-1.41</td>
</tr>
<tr>
<td>Cu</td>
<td>-2.63</td>
</tr>
<tr>
<td>Rh</td>
<td>-2.05</td>
</tr>
<tr>
<td>Pd</td>
<td>-2.01</td>
</tr>
<tr>
<td>Ag</td>
<td>-4.16</td>
</tr>
<tr>
<td>Ir</td>
<td>-2.45</td>
</tr>
<tr>
<td>Pt</td>
<td>-2.55</td>
</tr>
<tr>
<td>Au</td>
<td>-3.5</td>
</tr>
</tbody>
</table>

Table VII Weighted $d$-band centers for PdX alloys

<table>
<thead>
<tr>
<th>Pd-X alloy</th>
<th>Pd $d$-band center (eV)</th>
<th>X $d$-band center (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdCo</td>
<td>-2.79</td>
<td>-1.03</td>
</tr>
<tr>
<td>PdNi</td>
<td>-2.48</td>
<td>-1.05</td>
</tr>
<tr>
<td>PdCu</td>
<td>-1.82</td>
<td>-1.75</td>
</tr>
<tr>
<td>PdRh</td>
<td>-2.47</td>
<td>-1.69</td>
</tr>
<tr>
<td>PdAg</td>
<td>-1.60</td>
<td>-3.65</td>
</tr>
<tr>
<td>PdIr</td>
<td>-2.80</td>
<td>-1.86</td>
</tr>
<tr>
<td>PdPt</td>
<td>-2.23</td>
<td>-2.34</td>
</tr>
<tr>
<td>PdAu</td>
<td>-1.64</td>
<td>-3.22</td>
</tr>
</tbody>
</table>

In order to explain geometric effects and electronic effects, the XANES and density of states of PdNi and PdPt are presented in Figure 37 and 38.
Figure 37 PdNi XANES (left) and d-PDOS (right). Top: Pd edge. Bottom: Ni edge.

Graphic interpretation of the XANES L-edge as well as the d-Density of States is shown grouped by column or row of the periodic table in Figures 39 and 40. In all cases the depicted edge is that corresponding to Pd in the bimetallic.
We begin our analysis with an examination of PdPt and PdNi alloys. The phase diagram of PdNi and PdPt indicate that these systems are homogeneous alloys with fcc structures (i.e. the metals will appear randomly according to their relative concentrations and do not form special phases) \( (111) \) \( (112) \) \( (113) \). Alloying Pd with Ni shows that upon alloying of a 4d metal (Pd) with a smaller 3d metal there is a predicted narrowing of the \( d \)-band in the Ni and simultaneous broadening of the Pd PDOS in the alloy. This change in the PDOS can be attributed to geometric (strain) effects. Ni in a PdNi alloy is effectively in expansion since the bond distance of PdNi (2.63 Å Pd-Ni, 2.71 Å Ni-Ni) is larger than for bulk Ni (2.44 Å).

Experimental lattice parameters obtained from EXAFS K edge of Pd and Ni show a bond distance of 2.63 Å for PdNi and 2.49 Å for Ni (114) validating our model for PdNi and Ni bulk crystal structure which have bond distances of 2.61 Å for PdNi and 2.48 Å for Ni. This results in the observed narrowing of Ni PDOS. Conversely, Pd is effectively in compression (bond distance for bulk Pd is 2.79 Å) and its \( d \)-band is expanded. Since charge transfer between the metals is minimal and the relative filling of the \( d \)-bands for both Ni and Pd are virtually unchanged, the changes in the \( d \)-band shapes lead to shifts in the \( d \)-band centers from -2.01 eV to -2.48 eV for Pd and from -1.41 eV to -1.05 eV for Ni. Therefore, the strain effects in the PdNi system result in altering the reactivity such that Ni which is more reactive of the two metals becomes even more reactive upon alloying, and Pd the less reactive of the two metals, becomes even less reactive upon alloying.
Similarly, examining the XANES of the Pd L\textsubscript{2,3} absorption edge of PdNi shows that there is an increase in intensity in the Pd edge in the alloy as compared to pure Pd. In addition there is a slight shift of the edge for the alloy towards higher energy that could also be attributed to the contraction of the Pd lattice. The opposite effect is seen in the Ni edge, where alloying with a metal with larger lattice parameter has the effect of decreasing the XANES leading edge. As in the case of the density of states profiles for the \textit{d}-orbital, these changes are related to the strain effect that alloying imposes on this system. The increase in intensity for the Pd edge is related to the increase in hybridization that occurs due to the “overbonding” of Pd in the PdNi alloy. Similarly, Ni, which is effectively in expansion in the alloy, has more pure \textit{d} character since it is now underbonded and the XANES intensity decreases.

Similar shifts in the absorption edges and PDOS are observed for PdPt although one might expect that the shifts should be different. As the shifts in PdPt mirror those of PdNi, this would suggest that the driving force must actually be different (since obviously we would initially expect \textit{3d} and \textit{5d} metals to have opposite effects on Pd). Naively one could suppose that the Pd in a PdPt alloy is in expansion since the lattice constant of PdPt is larger than for plain Pd as mentioned above. This would result in a narrowing of Pd PDOS. Conversely, one could conjecture that Pt would respond as if it was in compression (and its \textit{d}-band would expand). In fact this is not the case. The Pt PDOS shows the narrowing of the \textit{d}-band for Pt in the alloy from -2.55 eV to -2.34 eV and a simultaneous broadening of the Pd PDOS in the alloy from -2.01 eV to -2.23 eV. We believe that this behavior results from the fact that Pt has a larger orbital extent than Pd. The orbital extent of Pd is 3.38 Å whereas Pt has an orbital extent of 3.79 Å (115). This implies that in the alloy, Pd is now “overbonded” by Pt and experiences
increased hybridization due to the larger overlap with Pt than it would have had with its Pd neighbors. Similarly, Pt is now “underbonded” by Pd since the d-orbitals of Pd do not extend as far as Pt.

These differences in extent are manifested by the large increase in the melting temperature of Pt with respect to Pd. Not surprisingly, the PDOS is completely consistent with the observed XANES as the decrease in the absorption edge of Pt in the alloy stems from the increase in pure d states due to the lack of hybridization in the alloy as compared to the pure metal. Of course, Pd follows the opposite trend as it experiences greater bonding in the alloy as opposed to pure metal. Experimental Pd L\textsubscript{3} and Pt L\textsubscript{3} XANES carried at beamline 9-BM by Bolin \textit{et al.} follow the same trends as the simulated XANES in which the Pd edge increases in intensity upon alloying and the opposite effect with a small shift to lower energy and lower intensity is seen on the Pt L\textsubscript{3} edge (116).
Figure 38 PdPt alloy XANES (left) and d-PDOS (right). Top: Pd edge. Bottom: Pt edge.
**PdX: X= 4d (Rh, Ag)**

Two distinct effects have now been identified: lattice effects and orbital extent effects, both of which affect the $d$-band center width and the degree of hybridization in metal-metal bonds. For the $4d$ metals, the orbital extents of their $d$-electrons changes only slightly (3.32 Å, 3.38 Å, 3.34 Å for Rh, Pd, and Ag respectively) in response to changes in the orbital filling (from 8 to 10 electrons). Therefore this row constitutes a nice case in which geometric effects are clearly seen. Both PdAg and PdRh form fcc homogeneous alloys at all concentrations. Rhodium has a lattice that is 2.8% smaller than that of Pd. In this contraction the $d$-DOS weighted center shifts from -2.01 eV for pure Pd to -2.47 eV for the Pd edge of PdRh. This shift is clearly reflected in the increase of the XANES edge with respect to pure Pd XANES. An opposite effect is seen when Pd is alloyed with Ag, where the Ag lattice is 5.1% larger than that of Pd. This expansion has a clear effect in the $d$-DOS. The center of the $d$-band is shifted by 0.41 eV towards the Fermi edge (from -2.01 eV to -1.60 eV). This also implies the Pd $d$ orbitals being further apart and thus less bonded and therefore, the Pd becomes more reactive and this is evident in the shift towards the Fermi edge. As expected, the XANES intensity of Pd in the alloy is reduced and shifts to slightly higher energy.

Now that we have established trends for a single column and single row involving Pd, we will examine how the remaining columns and rows of the PdX alloys for late $d$-band transition metals behave.
PdX X=$d^8$ (Co, Rh, Ir)

Alloying with Co, Rh or Ir implies a contraction for the Pd lattice on all three cases. For this group, all $d$-bands have shifted away towards lower energies from pure Pd at -2.01 eV to -2.79 eV for PdCo, -2.47 eV for PdRh, and -2.80 eV for PdIr. As explained previously, both orbital extent and lattice contraction may lead to changes in the PDOS (and XANES). This is clear when comparing the PdIr with PdCo or PdRh. Co is a 3d metal and has a M-M distance of only 2.44 Å. Therefore, Pd is in compression when alloyed with Co with an average M-M distance of 2.64 Å (considerably smaller than bulk Pd). The lattice constants for $d^8$ metals increases as we move down the $d^8$ column on the periodic table, thus it would be expected that the effect of lattice contraction should decrease. However, the $d$-band center of Pd in the PdRh alloy is less shifted than that of either PdCo or PdIr. This is an effect of orbital extent. In the case of PdRh, as noted above, the orbital extent of Rh is very close to Pd, so PdRh behaves very similarly to Pd in compression. However, in the case of PdCo, the orbital extent of Co is only 2.46 Å. Therefore, although Pd is in compression in that the M-M bond distance is dramatically reduced, the degree of orbital overlap is reduced as we shift from Pd to Co. The change in the PDOS is due to the dramatic difference in the lattice constant between Co and Pd. At the same time, the $d$-band center of Pd in PdIr experiences the same dramatic shift. Although the lattice constant for Ir is very similar to Rh, the shift in the Pd PDOS upon alloying is much larger in PdIr. In this case, the shift stems from the overbonding from the larger extent of the Ir $d$-orbitals (3.72 Å) (115). The effect in the XANES, implies that the degree of orbital overlap dominates over lattice constant changes as seen in Figure 39. For PdCo, contraction and orbital extent have counteracting effects. While the M-M bond contraction that is felt by the Pd in the alloy results
in an increase in the intensity of the XANES whereas the lack of orbital overlap due to the smaller orbital extent of the Co has the effect of diminishing the intensity of the XANES. The case of PdIr is in contrast with of the PdCo, in this case the effect of geometric strain and orbital extent work together to result in an increase in the intensity of the XANES. As seen in Figure 39, the density of states profile for both PdCo and PdIr are completely different although their weighted centers are very similar to each other and this difference in the shape of the DOS near the Fermi edge that is related to the changes on the XANES as discussed below.

\textbf{PdX X=d^{\text{10}} (Cu, Ag, Au)}

Moving to the X=d^{\text{10}} column, we find that the 3d metal, Cu has a much smaller lattice than Pd, but in contrast to d^{\text{8}} metals, the lattice parameters of Ag and Au now exceed that of Pd. Therefore, based upon arguments related to the lattice constant, one would expect that the Pd PDOS should be shifted away from the Fermi edge in PdCu and shifted towards the Fermi edge when Pd is alloyed with Ag or Au. However, the behavior of the PdCu is unique in that PdCu forms a bcc structure in phase diagram when the wt\% Pd is between 49\% and 60\% (117). For this unique case, we observe a shift in the PDOS of Pd in the PdCu toward the Fermi level (from -2.01 eV to -1.82 eV). In the case of PdAu and PdAg alloys, the lattice expansion in the alloy relative to bulk Pd, results in a shift in the Pd PDOS toward the Fermi level as expected (-1.60 eV for PdAg and -1.64 eV for PdAu).

Examining the simulated XANES intensity of Pd L_{2,3} edges of the PdAg and PdAu alloys a decrease in the intensity of the XANES is expected due to upshift in the \textit{d}-band center toward the Fermi level. Although expansion of the PdAu alloy is greater than that of PdAg by only 0.01
Å, there is a significant difference in the intensity of the XANES. We ascribe this difference to the large differences in the orbital extent of Au and Ag (0.54 Å). In the case of PdAu, the presence of Au results in some compensation effect for the lattice expansion and the decrease in the XANES intensity due to lattice expansion is counteracted partially by the increased overlap of Pd and Au as compared to Pd and Ag. Coulthard and Sham studied the intensity of the L₂ and L₃ with different ratios of Pd:Ag (118). It was seen that as the fraction of Pd decreases in the alloy, the intensity of the L₃ XANES decreases compared to that of Pd. For a 1:1 ratio of Pd:Ag, it is clear that the experimental data of the L₃ edge has the same trend as the data presented herein.

The case of PdCu is not easily explainable. According to the Pd PDOS calculations, the d-band center is shifted toward the Fermi edge following the trend of Au and Ag. However, in this case, we would actually expect the d-band center to shift away from the Fermi level since the Pd-metal bond distances in PdCu have decreased with respect to Pd. However, in the bcc structure of the 1:1 alloy, the Pd-Pd and Cu-Cu bond distances have both grown. In addition, the XANES shows a large increase in the intensity of the Pd L₂,₃ edge, which would be indicative of a case of an increase in the hybridization and the creation of unfilled states with d (or s) character. It has been suggested by Kitchin that the shift in the d-band center toward the Fermi level is due to poor overlap between the d-orbitals of Cu and Pd due to the differences between their PDOS. It is interesting to note that the d-band centers of both Ag and Au also shift toward the Fermi level when alloyed with Pd although strain effects would argue that the shifts should be in the opposite direction. In each of these cases, the resulting “molecular” orbitals arising
between Pd and the alloying metal result in shifts toward the Fermi level indicating destabilization of these orbitals.
Figure 39 PdX alloy XANES (left) and d-PDOS (right) for columns Co, Rh, Ir (top), Ni, Pt (middle) and Cu, Ag, Au (bottom).
Now that we have discussed the trends as a function of column and demonstrated the effect of orbital extent, we can go back and examine trends for PdX with X=3d and X=5d. Looking at PdX for X=3d late transition metal alloys, we have three cases of compression as well as orbital extents which are smaller than that of pure Pd. For this row, the lattice constants are 2.44 Å, 2.48 Å, and 2.57 Å and the orbital extents are of 2.46 Å, 2.46 Å, and 2.68 Å for Co, Ni, and Cu respectively. As explained in the previous section, contraction of the lattice will result in a shift in d-band center of Pd away from the Fermi level and this is indeed what we find for PdNi and PdCo from -2.01 eV for pure Pd to -2.79 eV and -2.48 eV for PdCo and PdNi respectively. However, as discussed above, PdCu does not seem to obey this trend. Similarly, we would expect that the lattice contraction (and therefore d-band widening) should result in an increase in the Pd L\textsubscript{2,3} absorption edge. A small increase is indeed observed for PdNi and PdCo. The simulated spectra for PdCu show a much more dramatic effect of alloying on the XANES. The result suggests that the increase is due primarily to the large increase in overlap between Pd and Cu as compared to PdCo and PdNi due to the significantly larger orbital extent of Cu as compared to either Co and Ni (and without a significant increase in the lattice constant).
Figure 40 PdX alloy XANES (left) and d-PDOS (right) for rows Co, Ni, Cu (top), Rh, Ag (middle) and Ir, Pd, Au (bottom).
Finally, for PdX, X=5d, we move to systems where the orbital extents are larger than that of Pd. Ir, Pt and Au have orbital extents of 3.72 Å, 3.79 Å, and 3.88 Å respectively (115). These larger extents convey a feeling of ‘overbonding’ to the Pd alloyed with them. However, the lattice constants of Ir, Pt, and Au vary significantly such that when Pd is alloyed with Ir, the metal-metal bond distance is compressed as compared to Pd and when Pd is alloyed with Au, the metal-metal bond distance is expanded as compared to Pd. This is observed in the Pd PDOS where the d-band center of Pd shifts away from the Fermi level when alloyed with Ir and toward the Fermi level when alloyed with Au. For the case of PdPt, as discussed above, the lattice constant of Pt is slightly larger than that of Pd, which would suggest an expansion of the lattice and a shift in the d-band center of Pd toward the Fermi level. However, the increase in the orbital extent of Pt compared to Pd, counteracts the lattice compression and results in a shift in the Pd d-band center away from the Fermi level. The simulated XANES of the Pd L₂,₃ edge follow this trend. There is a slight increase in the edge intensity in the PdPt alloy. A large increase in the edge intensity of Pd results from alloying with Ir due to the synergistic effect of lattice compression and increased overlap.

A case in which the orbital overlap and the lattice mismatch have opposite effects is seen in PdAu. As mentioned above gold has a larger lattice than Pd (resulting in underbonding) but also has a larger extent than Pd (resulting in overbonding). If both effects were of the same magnitude, one would expect the XANES edge to be in the same position of that of pure Pd.
The combined effect here (a loss of edge intensity) shows that the lattice expansion weighs more heavily than the increase overlap due to orbital extent changes.

An important observation of the row comparison is that orbital extent plays an important role in the intensity of the XANES as we move to the 5d metals. For all rows, a combination of both effects is observed in the behavior of the XANES and the ability to distinguish between both is related to the changes in the density of states of the \( d \)-band. Lattice effect, in general, seems to be more dominant in the 3d and 4d metals but one cannot predict the electronic structure (and resulting XANES) from the lattice parameters alone. This has been clearly illustrated in the previous work of Kitchin et al. In determining the \( d \)-band width, both the orbital extent and the interatomic spacing are pertinent. Incorporating lattice and orbital extent, Kitchin et al. proposed the following formalism to obtain the width of the \( d \)-band of bulk structures (Equation 2):

\[
W_{d,i} = W_{o,i} + \sum_j \left( \frac{r_d^{(i)} r_d^{(j)}}{d_{ij}^5} \right)^{3/2}
\]

Equation 2 \( d \)-band width (115).
$W_{o,i}$ is a constant to account for the atom $i$ non-zero band width at infinite separation.

$r_d^{(i)}$ is the orbital extent of atom $i$.

$d_{ij}^5$ is the distance from atom $i$ to neighboring atoms $j$.

It is also apparent from the discussion above that the location of the $d$-band center as a direct predictor of the absorption edge is not viable. The $d$-band center for Pd in PdCo and PdIr are nearly identical but the XANES intensity is quite different with the absorption edge of Pd when alloyed with Ir much larger than when alloyed with Co. One can also observe that the Pd PDOS have very different shapes in these two alloys. These differences are noticeable in the width of the $d$-band at different points of the profiles. At lower energy, the profile of PdCo drops in intensity prior to PdIr. The full width at half maximum of PdCo is 5.56 eV and for PdIr 5.23 eV. This difference of 0.33 eV is mainly due to the states closer to the Fermi edge of PdCo which are lacking on PdIr. However, although the $d$-band of PdCo is narrower, it does have a higher intensity than PdIr at most points below the $d$-band center. Difference in the Mulliken charges on Pd between PdCo and PdIr are insignificant (-0.05 for PdCo, and -0.01 for PdIr) implying the leveling of filling is the same. In this case, the $d$-band centers are nearly identical but the $d$-band widths vary, even though no charge transfer takes place. This example shows that the rectangular $d$-band model of Hammer and Norskov does not supply a complete description of the complex interactions between disparate metals. The differences in the shapes of the Pd PDOS for the two alloys gives rise to striking differences in their simulated XANES: a large increase in the leading edge for PdIr due to the increase in intensity of unfilled states above the edge related to the increased width of the band.
In addition to alloying with $d$-band transition metals, we can also consider the case of alloying with metals with fully filled $d$-bands whose valence electrons are $p$ electrons. Alloying with metals such as Zn, Ga, and Sn has a distinctive effect on the catalytic properties of Pd. We refer to these metals as $p$-electron metals. Iwasa and co-workers first noticed an improvement in the performance of methanol reforming catalysts by the replacement of Cu/ZnO by Pd/ZnO (30). Subsequent studies revealed that the activity of the catalyst was related to alloying between Pd and Zn (119; 120). Using XPS, Iwasa et al. observed a shift in the 3$d$ orbital of Pd to higher binding energy upon formation of the alloy (30). Partial formation of PdZn alloy can also be determined by EXAFS K edge (121) (119) (122). The same principle was also used by Grandjean et al. to determine formation of PdSn bulk phase alloy by using the Pd and Sn K edge (123) (124) (125). Another reaction with increased selectivity with PdSn phases is the hydrogenation of 1,3-Butadiene to 1-butene (125). In this catalyst the Sn changes the ensembles of Pd on the support by creating new Pd-Sn bonds which have the effect of increasing selectivity by approximately 25% at the same time as decreasing the formation of $n$-butene (unwanted product). Figure 41a depicts the simulated XANES for a series of PdX alloys (PdZn, PdGa and PdGe). The characteristic shift of the leading edge of the XANES and the change in intensity is not as noticeable as in some of the $d$-$d$ (PdAu, PdAg). The increase in the XANES edge follows the order of PdGa, PdZn, and PdGe and does not follow a clear trend with the position of the elements on the periodic table. The PDOS plot shown in Figure 41b gives an explanation to this result. The density of states of the $d$ orbital of Pd on the alloys is clearly shifting away from the Fermi edge.
As stated previously, the states close to the Fermi edge are closely related to the changes in the XANES. It is seen in the d-PDOS that close to the Fermi edge the available density is diminishing in the order of PdGe, PdZn, and PdGa. Depletion of the density of states and the shift of the Pd d-band towards lower energy implies there is a stabilizing factor of this orbital. In order to determine the origin of the stabilization of the Pd d-band in the alloy, a bader charge analysis was performed and a charge transfer from the p-electron to the Pd is seen. The charge being transferred follows the trend of Ga, Zn, and Ge with charges of -0.47 e⁻, -0.41 e⁻, and -0.29 e⁻ respectively. The same shift away from the Fermi edge was observed by Kovnir et al. when comparing Pd with PdGa in which interaction of Pd with Ga is shown to fill the d-orbital of the Pd thus shifting the center away from the Fermi upon alloying (126) (127). Pd L₃ edge of PdGa and Pd have similar intensity with a slight shift to higher energy upon alloying (~2 eV) as found

Figure 41 Pd alloys with p-electron metals Zn, Ga, and Ge. a) XANES. b) d-PDOS.
by Jeon et al. (128). Changing the ratio of Pd:Ga, they demonstrate that the intensity of the XANES increases at a 1:3 ratio while it decreases at a 2:1 ratio of Pd to Ga. Comparison of the intensity of our simulated spectra has a similar result. Both Pd and PdGa have approximately the same intensity varying mainly by a shift to higher energy by 2.3 eV (based on highest intensity point). Pt alloys with Ge (128) have also shown a similar trend to our simulated spectra of PdGe on both L$_2$ and L$_3$ edges in which, upon alloying, there is an increase in the leading peak of the XANES. The Bader charge analysis and PDOS suggest that there is charge donation of the p-electron to the d-metal. Due to the lack of states close to the Fermi edge, another orbital must contribute to the shift and intensity changes of the XANES. Taking a closer look at the palladium’s s-orbital on Figure 42, there is an increase in the density of states close to the Fermi edge that follows the trend of PdZn, PdGe and PdGa. A contribution of the empty states with s character seems to be responsible for the XANES changes. When alloying with p-electron metals, one should take into account not only the d-band states but the s states as well. The rules defined by the d-band model must be modified in instances where significant charge transfer occurs. This can be demonstrated by an examination of the adsorption strength of a test molecule such as CO on surfaces of these alloys. For example the d-band center of Pd in PdZn has been found to be very similar to Pt (Ed = -2.62 for PdZn and Ed = -2.55 for Pt). However, when CO is adsorbed on these surfaces, the adsorption energy decreases from Eads = -1.61 eV on Pt(111) to Eads = -0.98 eV on PdZn(111). Clearly this seems inconsistent with the d-band model. We suggest that this inconsistency lies with an implicit assumption of the d-band model: the d electrons have a continuity of states up to and above the Fermi level. In cases where the d-band is fully filled, this is no longer true. In the case described here with PdZn, the
Pd $d$ states are now fully filled and a depletion of states with $d$ character is present at the Fermi edge. This is also illustrated by the work of Rosch who similarly calculated the adsorption of CO on PdZn(111) and Cu(111) at a 0.25 ML coverage. Rosch et al., found that the adsorption energy was $\sim 0.9$ eV on both surfaces and that the two surfaces have similar $d$-band centers ($-2.44$ eV for Cu(111) and $-2.51$ eV for PdZn(111)) (31). In the case of comparing PdZn to Cu, the $d$-bands are both filled so the use of the $d$-band center as a descriptor seems to hold. However, caution should be applied in any case where the $d$-orbital PDOS intensity drops near the Fermi edge.

Figure 42 Pd alloy with p-electron metals s-PDOS.
3.4 Conclusions

It has been proven that different geometric changes to the Pd bulk when alloying have different effects on the XANES and can be explained by relating the intensity of it to the density of states near the Fermi edge. The positioning of the $d$-band center can potentially dictate the adsorption properties of an alloy, providing a useful tool to predict the behavior of the alloy for a distinct reaction. In some cases, the geometric effect has the same direction as the orbital hybridization effect. On other instances, these effects have opposing forces. The level of hybridization is related to the orbital extent and the bond distance between metals. When alloying with non $d$ transition metals ($p$-electron), other orbitals have a role in the shift of the XANES leading edge. Electronic effects tend to have a greater impact than that of geometric effects.
4 ELECTRONIC STRUCTURE OF CORE-SHELL ALLOY STRUCTURES OF Pd, Au, Pt, AND Cu

4.1 Introduction

Alloy nanoparticles can often take on different structures than what bulk thermodynamic calculations would suggest. In some cases, this stems from the specific synthesis method employed which creates a material which is trapped in a thermodynamically metastable state due to kinetic considerations. A common subcategory of alloy nanoparticles are core-shell alloy particles whereby the shell is enriched in one metal disproportionate to the overall composition and the core is similarly enriched in the other metal. Numerous computational studies have been undertaken to examine the formation of these core-shell systems and many more have taken on the task of examining how the physical structure leads to unique electronic properties in these systems. For example, Pretzer et al. performed a thorough study on the use of AuPd core-shell alloys to carry hydrodechlorination that could potentially be a green technology to treat groundwater (129). Using a reduction based method, three different sizes of core Au nanoparticles (3 nm, 7 nm, and 10nm) were dosed with Pd at different coverages forming a core-shell structure that was confirmed by STEM and XAS. Pd was found to form 2-D islands on the Au particles at low surface coverage and only formed 3D structures at Pd surface coverage of 70% or higher. These AuPd core-shell clusters were shown to be more active for the hydrodechlorination of trichloroethene. Plotting the reactivity against
the particle size revealed a classic volcano shape. A similar volcano plot could be constructed when plotting the reactivity against the Pd surface coverage (129).

Construction of core-shell nanoparticles is conventionally done by successive reduction of the precursors. The reduction method provides with the possibility of a wide range of particle sizes from smaller particles (1.2 nm- 4.2 nm well dispersed (130)) to larger particles in the range of 75 nm which have structures of onion like shells with an Au rich core (131). Variations of the reduction method also include ultrasonic irradiation (132), use of dendrimer structures as templates (133), and aided reduction by the support (134) among others. Other methods that are not as widely used are Pd electrodeposition on Au nanoislands of 100 nm (135), galvanic replacement reaction between Pd nanowires and Au precursor (136), and combined digestive ripening and seeding growth (137). Annealing of core-shell alloys (i.e. heat treatment in air at 500˚C (134)) has been reported to result in the formation of random alloys. AuPd alloys have been used for the hydrogenation of cyclohexane (132), CO oxidation (138), the direct oxidation of benzyl alcohol to benzyl aldehyde (139), the hydrogenation of O₂ to form hydrogen peroxide (140), and as direct methanol fuel cell anode catalysts (141).

Beyond AuPd core/shell catalytic nanoparticles, there are a vast number of possible core-shell structures each with its own unique reactivity. Therefore, an improved understanding of such structures would guide us to produce new catalysts with higher activity and selectivity. PdPt alloys are another interesting catalytic system. Although Pt and Pd are in the same column of the periodic table, PdPt alloy nanoparticles have been shown to possess unique reactivity (57) (142) (143) (144). There are several methods to synthesize Pd-Pt core-shell alloys with
different sizes and shapes. Through a sacrificial hydrogen layer method, Sanchez et al. synthesized PdPt and PtPd core shell alloys with shapes of icosahedron for the Pd core and nanocubes with a Pt core. The particles are reported to have sizes of 2 nm to 4 nm (145). These core-shell nanoparticles based on Pd and Pt are good candidates for direct methanol fuel cell anodes. (146). Among the most popular methods to synthesize core-shell nanoparticles is precursor reduction deposition starting with a metal seed (147). Long et al. used silver nitrate as a structure directing agent achieving Pt-Pd core-shell particles of 10 nm – 20 nm and varying the precursor quantity to control the thickness of the shell. Similar to other metals, Pd grows preferentially on low index planes such as (111), (100), and (110) (146). With the presence of a single layer of Pd on Pt, the binding energy of OH shifts slightly, improving the catalytic activity for cathode (i.e. oxygen reduction) for PEM or direct methanol fuel cells as compared to monometallic Pt electrocatalysts with similar morphology (146). Nanoplates have also been synthesized in a core-shell manner. For both hexagonal and triangular Pd nanoplates, Lim et al. have dosed Pt by reduction with citric acid to synthesize nanoplates with epitaxial growth of Pt on Pd with edge lengths in the ranges of 50 nm up to 100 nm (147). Slow reduction is crucial to the nucleation of the nanoparticles and the speed of the reduction process provides another variable to control growth. Hydrogenation of methyl acetate has also seen an improvement in activity with PtPd core-shell alloys as compared to Pd nanoparticles (144).

Core-shell nanoparticles have been shown to be versatile and thus possess the ability to be tuned to required characteristics. For example, Somorjai’s work with RhPd and PdPt core-shell structured alloys show that by changing the environment of the nanoparticles, it is possible to alter the composition of the shell. In the case of RhPd, changing between oxidative
and reducing conditions results in a restructuring of the surface that is reversible in which the shell is either Rh rich (oxidizing conditions) or Pd rich (reducing conditions) (148). In contrast, PdPt alloy does not display this reversible restructuring and in fact always has a Pd rich shell that under oxidation forms PdO and under reduction it maintains a Pd rich shell with no major segregation. Obviously in the case of PtPd the difference in surface energy between the metals is lower than that between Rh and Pd. For proton exchange membrane fuel cells, the oxygen reduction reaction is extremely important and PtPd core shells have been shown to be more active and more durable than commercial Pt/C catalysts (149). A database containing 340 (constructed by cluster expansion and truncation) states of a 55 atom octahedron cluster in which the content of Pt is varied from 0% to 100% in different positions of the particle, has shown that a core-shell configuration is among the ground states for a 55 atom cluster and hydrogen adsorption also varies in strength depending on the composition of the surface giving another variable for catalyst tuning (150). Recently, Lei et al. proposed the use of atomic layer deposition to produce extremely small nanoparticles (1 nm to 2 nm) with core-shell configurations. These core-shell nanoparticles where shown to have improved selectivity as well as yield to the desired product, propylene, in the oxidative dehydrogenation of propane when compared to monometallic mixtures of Pd and Pt also produced by ALD (143).

Another alloy system which has been studied is PdCu for electrocatalytic oxygen reduction. Using density functional theory, Henkelman et al. have shown that Hammer and Norskov’s d-band model can be used as a reactivity indicator for the oxygen dissociation on PdCu core-shell alloys (151). In addition, there is a linear trend between the oxygen binding energy and the ratio of Pd:Cu in the core of the alloy, reaching an optimal composition of 42%
Palladium-copper alloys in the form of core-shell can be produced by galvanic replacement reactions in which the difference in electrical potential of the metals is used as driving force for the deposition (153). With this method, Xie et al. have produced nanocubes with edge distances ranging from 45 nm to 100 nm. The effect of varying the current on the electrochemical deposition to control particle size has been studied by Alvarez and Salinas by deposition of Pd onto vitreous carbon using a PdCl\(_2\) solution and consequent deposition of Cu\(^{2+}\) (154). The study determined that there is a progressive nucleation of the Pd nanoparticles whose kinetics are related to the potential used. Lattice mismatch is a determining factor in the way the core-shell alloy is produced by seed growth. Jin et al. propose that, for alloys with a mismatch over 5%, epitaxial growth is preferred and there is a lack of control on the shell thickness and the particle shape (155). Due to the lattice difference between a pure Pd and a pure Cu (8% lattice mismatch), the growth of Cu on Pd seeds happens in an epitaxial manner and control of particle size and shape is difficult. Particle size can then be controlled by the amount of Pd seeds used, achieving sizes of 50 nm, 75 nm, and 100 nm. Another method of preparation of the core-shell PdCu nanoparticles is presented by Suresh et al. using stepwise impregnation of Cu and Pd onto TiO\(_2\) (156). By varying the precursor used, they determined that chlorides are best since the deposited Pd is metallic in nature unlike nitrates in which the palladium tends to be PdO. Control of the particle size can be done by thermal treatment under reducing conditions to yield larger particle sizes (156). In oxidizing atmospheres it is possible to separate the metals in the alloy by heating and oxidizing the Cu to CuO, which also happens in the AuCu core-shell alloy (157).
Systems such as AuCu are subjected to an extreme lattice mismatch. Regardless of the difference in lattice parameter, it is possible to produce a core-shell particle by epitaxial growth of Cu on Au core. Using Au nanoparticles as templates, Alam et al. have grown Cu and other metals on these particles with preferential growth on the Au(111) planes with a shell thickness of approximately 30 nm (158). Selection of the shell metal is done based on lattice parameter, electronegativity, and bond strength of the metal with itself. In a similar manner, Liz-Marzan et al. have produced core-shell nanoparticles using Au seeds to avoid nucleation and have grown the Cu shell based on Cu2+ reduction with hydrazine (159). These nanoparticles are attractive to the fields of electronics and catalysis (160) as well as for an immunoassay for fast detection of E. Coli (161). Another method of experimentally producing these types of alloys is by using a magnetron sputtering gas condensation cluster beam which allows for controlled particle size, especially below 100 atoms, as well as reversing of the metal on the shell or core by controlling the pressure of the condensation gas (162). Low pressure of the condensation gas (1:2 He:Ar) produced cores rich in Cu and shells rich in Au. By simulating the intensity of the experimental STEM with different surface compositions, Yin et al. found that the profile that closest resembles the experiment is that of a Cu/Au core/shell structure. Reversing the core/shell composition can be done by increasing the pressure of the gas from 0.34 mbar to 1.0 mbar and increasing the He:Ar ratio to 5:2. This mass-selected beam method produced particles with sizes of 3.78 nm for the high pressure samples and 3.32 nm for the low aggregation pressure samples. The pressure and composition of the aggregation gas was deemed to alter the growth of the seed clusters, which need to reach a critical size to become stable, by cooling the
sputtered atoms that form the seeds. This opens a door to controlling the composition of the core-shell alloys by changing the condensation gas conditions accordingly (162).

Systems with more than one element can present surface segregation in which one metal migrates preferentially to an area of the particle depending upon environmental conditions. Yang et al. studied segregation in bimetallic particles using molecular dynamics corrected Monte Carlo simulations with particles varying in size (201 to 1289 atoms), and compositions with mole fractions varying from 0.1 to 0.9 for mixtures of Rh, Ni, Pd, Cu, and Ag, at various temperatures (200 K, 600 K, and 1000 K) (163). Overall, segregation is assigned to an interplay between two forces: surface energy and cohesive energy. Traditionally, a metal will segregate to the surface if it possesses a lower cohesive energy. However, in the case of Rh-Pt clusters, the metal with lower cohesive energy (Rh) actually stays in the core and Pt segregates to the surface due to its lower surface energy. Metals with the lowest surface energy have segregation trends that follow a path in which they segregate to low coordination sites that have higher amounts of available sites for the segregated metal (such as edges), stronger and then segregate to other surface sites, such as surface planes which have lower amount of regions with segregation sites, which minimizes free energy. Larger size particles were shown to have a higher dependence on temperature for the segregation. This behavior was attributed to a decrease in geometric constrains as particle size increases since they have more low coordination sites that are populated preferentially by the segregating metal (163). Particle sizes can reach a limit in which a vast majority of atoms can be considered to be at the surface (below 1 nm) (164). This can become an issue for characterization of segregation in nanoparticles even for larger sizes. Sault studied this critical size by modeling XPS spectra of Cu-
Ni, Pd-Cu, and Pd-Ag alloys at sizes ranging from 1 nm to 64 nm (164). As expected, signal strength of the core metal is dimmed by the increase of the segregating metal. Detection of segregation by XPS was determined to have a critical size below which no detection of segregation can be made between the sizes of 3 nm and 8 nm depending on the nature of the metal and the concentration at which complete segregation is achieved, thus the detection size decreases as the concentration of the segregating metal increases and it depends on the preferential segregation uniformity (i.e. support interaction might alter the segregation pattern thus making segregation not uniform and increasing the critical size to 8 nm). In addition, the support might influence the way segregation takes place by favoring interaction with one metal and preventing uniform segregation (164). Another factor that can influence segregation is the methods of pretreatment which typically involve calcination and reduction at elevated temperature Wanjala et al. examined annealing of 55 atom clusters of AuPt by using DFT and MD and compared the results of experimentally synthesized Au-Pt nanoparticles of sizes ranging from 1.6 nm to 3.4 nm (165). Heat treatments were carried at 400°C and 800°C for 30 minutes and 60 min with H₂ as reducing agent. The computational model and XPS agree on the segregation of Pt into the core of the alloy forming a core-shell structure. Segregation due to increases in temperature is dependent on fractional composition of the metals as well as time of the thermal treatment (165).

In this work we will examine how the presence of a core-shell structure will lead to changes in the electronic structure of the material. We will examine a few prominent examples: AuPd, PdCu, PdPt, and AuCu.
4.2 Methodology

A simple model was adopted to simulate core-shell alloy nanoparticles. A (111) plane surface with six layers was proposed as the model. In this model, the top most layer is replaced with the metal that is used as the shell and the remaining layers are considered to be the core. For comparison purposes, a bilayer model was constructed to simulate thicker shells. In this second model, the first and second top most layers are replaced for the shell metal and the four remaining layers are left as the core. An example of the model is shown in Figure 43. In all cases, the top four layers of the slab have been allowed to relax without allowing the lattice of the core to change in magnitude. The bottom two layers have been fixed to simulate bulk conditions towards the center of the core-shell particle. The following systems have been considered: Pd-Au, Pd-Pt, Pd-Cu, and Cu-Au.

![Figure 43](image_url) Representation of the monolayer replaced on host metal (left) and the bilayer replaced on the host metal (right). Cu on Au used to represent all cases.
Positions of the $d$-band center have been estimated by a weighted average considering all filled and unfilled states in the energy range of $-10$ eV to $10$ eV.

4.3 Discussion

Pd-Au

In our previous study of bulk PdX alloys, we observed that Pd was largely underbonded due to lattice expansion of 2.68% (DFT predicted Pd-M bonds expand from 2.79 Å to 2.87Å). In the case of the core-shell alloys with a Pd shell above a Au core the expansion-contraction effects are seen in different proportions in the $xy$ (parallel to the surface plane) and $z$ (normal to the surface plane) directions. For a Pd monolayer on Au(111) the distance between Pd-Pd is 2.95 Å, a 5.65% expansion of the Pd lattice in the $xy$ plane. In the $z$ direction, the Pd atoms are 2.84 Å away from the underlying layer of Au atoms. This also means that there is an expansion in the $z$ direction of 1.50% with respect to the palladium bulk distance, but contraction with respect to the optimal Pd-Au distance from bulk PdAu.

This result is not surprising since the creation of the surface requires that the atoms in the surface layer (CN=9) are undercoordinated with respect to the bulk (CN=12). This undercoordination has been shown by Hammer and Norskov to have a contraction in the width of the $d$-band density of states. The shifts in the $d$-band center lead to well documented changes in reactivity (3) (4) (166). The surface layer of metal surfaces is frequently contracted in the $z$-direction as the system seeks to minimize its free energy and stabilize its valence orbitals (167) (168).
In the model for the core-shell alloy, the presence of the gold underneath the Pd monolayer means that the Pd atoms are 3-fold coordinated to gold atoms and 6-fold coordinated to Pd (in the xy plane). In the core-shell alloy, the Pd-Pd bond distance is in expansion in the xy plane, meaning that the Pd is effectively undercoordinated compared to a Pd(111) slab. In addition, the Pd-M distance is expanded the z direction compared to a Pd(111) slab. However, in this case, there is also an orbital extent effect that arises from the much larger orbital extent of Au (as a 5d metal) compared to Pd. The orbital extent of bulk gold is of 3.88 Å and that of palladium is 3.38 Å (115). Therefore, Pd is overbonded in the z-direction due to the increased overlap. These two effects combine to result in an upshift of the Pd d-band center with respect to the Pd(111) slab (-1.29 eV vs. -1.64 eV).

Ignoring the orbital extent of gold and looking at the geometric effect in the z direction, we can expect a Pd-Au distance greater than that of a Pd-Pd if that second Pd atom was in the position of the gold. In fact, the distance between the Pd layer and the Au layer is 2.84 Å, which is greater than that of the top and second layer of the optimized Pd(111) slab of 2.80 Å. Comparing the Pd monolayer on Au(111) to the bulk, the z distance is actually decreased in the surface model by 0.03 Å (2.87 Å bulk Pd-Au distance). This slight contraction is probably due to the undercoordination of Pd and its need to stabilize itself by bonding. As mentioned in chapter 2, contractions in the lattice will frequently result in a shift of the center of the d-band away from the Fermi edge.
In order to separate the effect of changing the nature of the second layer element, calculations replacing the atoms of Au by Pd and selectively fixing the coordinates were carried out. In Figure 44, the models portrayed have the same starting structure as the Pd-ML/Au(111) but the atoms are all Pd and they have been fixed in the xyz directions (green) and on the xy leaving z relaxed (blue). The distance between Pd atoms in the xy plane are set to 2.95 Å and in the z direction from the first layer Pd to the second layer Pd to be 2.84 Å for the model fixed on xyz. The $d$-band center also shifted from -1.64 eV, for an unstrained Pd(111) slab to -1.35 eV due to the undercoordination in the xy direction. In fact this is slightly less than the shift for the
PdAu case, showing that the strained Pd-Pd interaction between the first layer of Pd and the second layer of Pd is even a bit stronger than the interaction between Pd and Au at the same distance. Fixing the xy plane and relaxing the z direction shows a contraction when compared to the original Pd-ML/Au(111). In this model, the top layer of Pd is at a distance to the second layer of Pd of 2.76 Å. This contraction from the original Pd(111) first to second layer of 2.80 Å reflects the compensation of the Pd expansion in the xy plane to 2.95 Å. The shift of the d-band center of the all Pd model with only the xy distances fixed is 0.10 eV away from the Fermi edge (Ed = -1.45 eV) when compared to the calculation where the distances are xyz fixed calculation. This difference in stabilization of the d-orbitals is expected due to the allowed relaxation (contraction) in the z direction of the latter model.

Alternatively we can also explore the effect of lattice expansion and contraction by examining the changes in the d-band center when perturbing a Pd(111) slab. Figure 45 shows Pd(111) with xy expanded to the Au(111) xy distance in green and the one with z expanded to Au(111) in blue. When examining the Pd(111) slab expanded in the xy plane, the in plane Pd-Pd distance is 2.95 Å and the Pd-Pd distance in the z direction is 2.80 Å. The PDOS indicates that upon expansion, the center shifted from -1.64 eV for Pd(111) to -1.41 eV for the Pd(111) expanded in the xy direction. In contrast, expanding the Pd(111) slab in the z-direction to the spacing of Au(111) shows a smaller effect (a shift to -1.51 eV) since bonding to only 3 nearest neighbors is affected in this case.

Now looking at the orbital effect, it is expected that due to the fact that the Au orbital extent is greater than that of Pd by 0.5 Å there will be a greater overlap of the gold’s d-orbitals.
with those of Pd. This increase in the overlap may result to a greater hybridization of the orbitals when compared to the pure Pd-Pd case. This increase in hybridization will shift the d-band center by changing its shape in order to preserve the filling of the d-band as explained by Linic et al. (169). This change in shape will actually be an expansion of the width of the d-band profile with a subsequent shift of its center towards negative energies. This shift away from the Fermi edge will result in an increase in intensity, thus counteracting the lattice expansion effect.

Figure 45 Density of states profile of the d-band for Pd(111), Pd monolayer on Au(111), Pd(111) expanded in the x and y direction to Au(111), and Pd(111) expanded on the z direction to Au(111).
The overall picture shows the dominance of the lattice effect over the orbital extent in this configuration. The width of the PDOS of the $d$-band is clearly reduced and shifted towards the Fermi level. In other words, due to the expansion of the palladium lattice, there is a reduction in the orbital overlap and therefore palladium is now less stable and more reactive.

As mentioned above, we also examined core-shell configurations where the top two layers are of the Au(111) surface are replaced by palladium. The PDOS of Pd in a bilayer shell above Au(111) is shown in Figure 46. Each layer displays slightly different electronic structure. The top most layer will still be undercoordinated and in expansion in the xy plane but it is now bonded to Pd underneath as opposed to Au. The second layer will not be undercoordinated (it has 9 Pd neighbors and 3 Au neighbors) but it will be in expansion in the xy plane. Both layers retained the distance of Au bulk (2.95 Å) in the xy plane but the atom positions will change in the $z$-direction upon optimization to achieve an energetically favored distance. For the first layer of Pd, there is a shift of the center of the $d$-band away from the Fermi level when comparing with the Pd monolayer on Au(111). This shift is from -1.29 eV for Pd monolayer on Au(111) to -1.39 eV for the first layer of Pd of the Pd bilayer on Au(111). The difference between both cases of the monolayer and the bilayer is due to the change in the bond distance in the $z$ direction and the nature of the element of the second layer. Gold is known to be inert, and in the case of the bilayer the top palladium atoms are coordinated to palladium not gold as in the case of the monolayer. The difference in the identity of the element of the second layer is seen in the contraction of the bond distance, which for the Pd-Pd distance of the bilayer on Au(111) is 2.77 Å, even lower than that of a pure Pd(111) Pd-Pd distance of 2.80 Å for those same layers. This contraction is expected since the top layer of Pd would hold on tightly to the
second layer of Pd that is also being ‘rejected’ by the Au underneath it. In other words the Pd in the second layer forms a stronger Pd-Pd bond to Pd in the first layer in the core-shell configuration than it does in a Pd slab due to its desire to maintain a certain level of bonding. In this case, replacing a Pd-Pd bond with a weaker Pd-Au bond results in an increase in the bond strength of all the remaining Pd-Pd bonds. The shortened bond distance also means that there will be a greater overlap (i.e. hybridization) as compared to the pure Pd-Pd case. This overlap explains the 0.10 eV shift in the d-band away from the Fermi as compared to the Pd monolayer over Au(111).

The second layer of the Pd bilayer on Au(111) shows somewhat different behavior. This layer is in expansion in the xy plane. In the z direction, this layer also experiences an expansion. With a distance from the Pd layer to the Au layer of 2.84 Å, the expansion of this layer is comparable to that of the Pd monolayer on Au(111) (2.84 Å in the z direction). The main difference between this layer and that of the monolayer case is the atoms surrounding the Pd. In the bilayer model, we now have 3 extra Pd atoms coordinated with the atoms in the layer of interest. However, the expansion does reflect on the position of the d-band center, which in comparison to a pure Pd(111) slab is shifted towards the Fermi edge. As in the case of the top layer on both Pd monolayer and the second Pd layer of the bilayer on Au(111), there is a shift of 0.40 eV, which seems to be associated with the identity of the atom to which the layer is coordinated. In the case of the second layer of Pd, coordination to gold in the layer beneath it seems to be associated with a shift of the d-band center towards the Fermi level.
Figure 46 Density of states profile for: the surface layer of Pd(111) and first layer of a bilayer Pd shell above Au(111) (left). PDOS of the second layer in a Pd(111) slab and the second layer of the bilayer Pd shell above Au(111).

**Pd-Cu**

The system of palladium copper alloy has a similarity to the PdAu, in which the host metal is inert. The main difference is that Cu, unlike Au, has a smaller lattice constant than Pd. In the bulk, Cu-Cu bond distances are 2.57 Å, about 8% smaller than Pd-Pd bulk distances. When constructing a CuPd core shell alloy, this bond distance is conserved in the xy direction after optimization of the new structure such that Pd is in compression in the surface layer.

By replacing the top layer of a Cu(111) slab with Pd and re-optimizing it, we can get an opposite lattice effect of that of the PdAu system. On the top layer, Pd adopts the lattice of Cu and it contracts in the z direction as well to 2.67 Å. Upon contraction, there is a greater Pd-Pd d-
orbital overlap. The increase in the orbital overlap in the xy direction also explains the broadening of the d-PDOS of Pd as seen in Figure 47. The broadening also means there is a shift of the d-band center towards lower energies (from -1.64 eV to -2.18 eV) due to the Pd ‘overbonding’ with itself. In the case of the Pd monolayer on Cu(111), the Pd atoms are bonding in the z-direction to Cu which has a noticeably smaller orbital extent (2.68 Å as compared to 3.38 Å for Pd). This interaction results in reduced hybridization in the z-direction. Overall, the lattice contraction is the main influence in the hybridization of the Pd d-orbital. The density of states profiles for the bilayer of Pd on Cu(111) are depicted in Figure 48. For the bilayer of Pd on Cu(111), the first layer of Pd has only a strain effect (i.e. no ligand effect is present). The strain effect can be partitioned into a lattice contraction effect in the xy plane and an expansion in the z direction. The xy contraction means that the Pd will increase its hybridization on the xy plane but in the z plane, there is actually an expansion when compared to Pd(111) distance of the top layer to the second layer. For an unstrained Pd(111) surface, the distance from the first to the second layer is 2.80 Å. However the distance between the first and second layers in the Pd bilayer on Cu(111) is 2.88 Å. This expansion seems counterintuitive initially based upon the arguments made for PdAu (i.e. bonding between the two Pd layers was stronger due to the weak Pd-Au bond). However, this expansion in the z-direction is actually a response to the extreme contraction in the xy plane. In other words, Pd first layer is trying to compensate for the overbonding that it feels due to the increased hybridization on the xy plane. Since the increased hybridization has been shown to have a shift of the density of states profile away from the Fermi level towards lower energy which also means the atoms are less reactive, and also that they will be prone to move away from the second layer. The expansion in the z
direction, keeping in mind that the layer underneath it is also Pd, is a pure geometric effect. The result is a $d$-band that is shifted away from the Fermi level by -0.40 eV, slightly less than the shift for the Pd monolayer on Cu(111), as in that case there is not a counteracting effect of expansion in the $z$ direction.

For the second layer of the Pd bilayer on Cu(111), the distance of the second layer of Pd to the next Cu layer is 2.69 Å which means that the hybridization of Pd with Cu $d$-orbitals is minimal. Compression of the Pd-Pd bond distance results in a shift of the density of states profile to lower energy. The shift when compared to that same layer on a Pd(111) surface is -0.50 eV. This shift is very similar to the one of Pd monolayer on Cu(111) which has a similar scenario when it comes to coordination to the Cu atoms in the layer underneath.
Figure 47 Density of states profile for the surface layer of Pd(111) and a monolayer of Pd above Cu(111).

Figure 48 Density of states profile for: the surface layer of Pd(111) and first layer of a bilayer Pd shell above Cu(111) (left). PDOS of the second layer of Pd(111) and the second layer a bilayer Pd shell above Cu(111).
Reversing the host metal and the replacement metal puts copper in an expansion. This expansion is from 2.57 Å to 2.79 Å in the x and y directions and 2.55 Å to 2.62 Å in the z direction. Figure 49 shows the shift in the PDOS of Cu when placed as a single layer shell above Pd(111). It is clear that the expansion results in a depletion of states in the d-band and thus the shift from -2.55 eV to -1.74 eV of the center of the d-band. Figure 50 shows the PDOS profiles of Cu in the bilayer shell structure above Pd(111). The bilayer Cu on Pd(111) has the same expansion as the monolayer case in the xy plane but instead of an expansion in the z direction, now there is a contraction from 2.55 Å for a Cu(111) to 2.51 Å from the first layer to the second layer of Cu, most likely due to the second layer of Cu pulling the top layer down towards it to compensate for the expansion. The effect of the compression, which would also translate in a shift of the density of states center away from the Fermi edge, seems to be overcome by the expansion in the xy plane. In comparison with the monolayer of Cu on Pd(111), it is clear that the bilayer case has a lesser shift in the position of the d-band center. For the monolayer, there is a shift toward the Fermi edge of 0.81 eV compared to a pure Cu slab while for the bilayer structure, the second Cu layer has a shift of 0.35 eV in comparison to the same layer in a Cu(111) slab. Both of the mentioned layers are undergoing expansion on the xy and z direction, so the main difference becomes the coordination number in which the monolayer is only coordinated to six copper atoms and three palladium, whereas the bilayer is coordinated to three more copper atoms which would help towards the stability of the layer and thus the decrease in the shift towards the Fermi level.
Figure 49 Density of states profile for Cu(111) and monolayer of Cu above Pd(111).

Figure 50 Density of states profile for: the surface layer of Cu(111) and first layer of a bilayer Cu shell above Pd(111) (left). The PDOS of Cu(111) and second layer of the Cu two top layer replaced Cu(111).
Unlike the Pd-Au or Pd-Cu systems, in which the host slab is inert, the Pt host is more reactive due to the fact that Pt does not have a completely filled $d$ orbital. In this case we will have expansion as in the case of gold but the lattice mismatch is small as the Pt-Pt bond distance in bulk Pt is 2.77 Å Pt as compared to 2.75 Å for the Pd-Pd bond distance in bulk Pd. Based upon a simple argument of lattice expansion, one would expect that the $d$-band would shift toward the Fermi edge due to the lack of hybridization. However, looking at Figure 51, the change in the center of the $d$-band is actually in the opposite direction as the $d$-band center moves to -1.73 eV whereas the $d$-band center of the surface layer of Pd(111) is -1.64 eV. Compared to a Pd(111) slab, the Pd monolayer on Pt(111) is expanded on the $x$ and $y$ direction by 0.02 Å and by 0.01 Å on the $z$ direction. The observed changes in the $d$-band center are not therefore due to changes in the metal-metal bond distance but rather due to the large difference in orbital extent between Pt and Pd by 0.41 Å. This means that Pd, now coordinated with Pt, has a greater overlap of the Pt $d$-orbitals than it would when forming a Pd-Pd bond. This overlap increase will shift the $d$-band center away from the Fermi level and since the level of expansion is negligible, the shift can be partially attributed to the increased orbital extent of Pt overbonding Pd.
Figure 51 Density of states profile for the surface layer of Pd(111) and a monolayer of Pd above Pt(111).

Figure 52 Density of states profile for the surface layer of Pd(111) and first layer of a bilayer shell of Pd above Pt(111) (left). PDOS of the second layer of Pd(111) and the second layer of a bilayer shell of Pd above Pt(111).
The results of the projected density of states for Pd in bilayer shell structure above a Pt (111) slab are shown in Figure 52. For a bilayer of Pd above Pt(111), the first layer is no longer bonded to Pt. In this case the expansion on the x and y direction is still 0.02 Å and the distance from the second Pd layer is of only 0.002 Å difference of a first layer to second layer Pd(111) surface. It is clear that this layer has a negligible expansion on the z direction and since there is no Pt underneath it, we have potentially isolated the expansion effect in the xy direction by eliminating the effect of coordination to a different element. The d-band center of the top most layer of Pd bilayer on Pt(111) has virtually no shift (-1.63 eV for the bilayer and -1.64 for the Pd(111)). On the density of states profile, the d-band center only shifting by 0.01 eV towards the Fermi edge corroborates the exclusion of geometric effects that had been done on the assignment of the shift on orbital extent and coordination on Pd monolayer on Pt(111).

The second layer of the Pd bilayer on Pt(111) is now coordinated to nine Pd atoms and three Pt atoms. The distances, after optimization, are expanded in all three directions. In the xy plane, the expansion was of 0.02 Å and 0.005 Å in the z direction, when compared to the same layer of a Pd(111) surface. In this case we have very similar expansion effects as in the first layer of the bilayer Pd on Pt(111) in which they are negligible, but in addition, we now have coordination to a metal with a different orbital extent (i.e. a ligand effect). As in the case of monolayer Pd on Pt(111), this layer has a considerable overlap with the Pt that is coordinated to it in the layer below it. The increase in d-orbital overlap results in a shift of the d-band center away from the Fermi edge from -2.01 to -2.04 eV.
The reverse case was also modeled in which the host is Pd(111) and the top layer is replaced by Pt. When replacing just one layer of the Pd(111) for Pt, the optimized structures has the x and y distance of the bulk Pd (2.79 Å) which translates into a contraction of the Pt which in a Pt(111) slab it would have a distance of 2.81 Å although there is a simultaneous expansion in the z direction of 0.01 Å compared to Pt(111). The density of states profile for the Pt monolayer above Pd(111) is shown in Figure 53 in comparison to Pt(111). Lattice contraction generally implies that the density of states profile would expand and shift away from the Fermi level. However, here we observe a shift in the Pt PDOS towards the Fermi of 0.06 eV (from -1.95 eV to -1.89 eV). Similar to the case of Pd monolayer on Pt(111), the current configuration has geometric changes that are not of considerable magnitude and the observed shifts can be ascribed to ligand effects. The shift of the d-band center is due to the difference in orbital extents between Pd and Pt, as Pt is now underbonded since the overlap between Pd and Pt is lower than that between Pt and Pt at the same distance.

In order to further understand the ligand effect we can look at the PDOS of Pt of the first layer of the Pt bilayer on Pd(111) shown in Figure 54. This layer is coordinated to nine Pt atoms, unlike the layer of the Pt monolayer on Pd(111) which is coordinated to six Pt atoms and three Pd. We see an expansion in the z direction, since the distance of this layer to the second Pt layer is 2.85 Å, (0.02 Å larger than for the monolayer Pt above Pd(111)). In summary, for the top layer there is an expansion in z and a compression in xy which results in a shift of the d-band center of Pt to -2.05 eV. Compared to the monolayer of Pt on Pd(111) the main difference resides in a ligand effect since the shifts in the lattice (both expansions and contraction) are very small. The removal of the ligand effect (since Pt is now bonding to the underlying Pt in the
second layer) results in a shift of the Pt PDOS away from the Fermi edge by -0.10 eV which can then be attributed directly to the lattice contraction in xy plane. For the second layer of Pt above Pd(111) (sublayer of Pt on Pd(111)), Pt is in contraction a contraction in the xy plane. In the z direction, the bilayer model has a distance from the second layer (Pt) to the third layer (Pd) of 2.79 Å as well. The d-band center presents an even greater shift away from the Fermi edge to -2.45 eV for this second layer of the Pt BL/Pd(111), since the contraction would have shifted the center of the d-band towards negative energy.

Geometry seems to not be greatly affected by the changes in the substrate of Pd or Pt as seen by the small expansions and compressions presented upon optimization. For this system, the orbital extent is the primary driving force for the observed shifts in the position of the d-band center.
Figure 53 Density of states profile for the surface layer of Pt(111) and a Pt monolayer of Pt above Pd(111).

Figure 54 Density of states profile for the surface layer of Pt(111) and first layer of a bilayer Pt shell above Pd(111) (left). PDOS of the second layer in Pt(111) and second layer of a bilayer Pt shell above Pd(111).
The copper gold system has two outstanding characteristics, first they possess extremely different lattice constant. Copper’s lattice in a bulk structure is 13% smaller than that of gold. Also, both metals have fully filled d-bands. A monolayer of Cu on Au(111) places the copper under extreme expansion. When compared to the same layer of a Cu(111) slab, the copper present on the top layer is being expanded from 2.57 Å to 2.95 Å in the x and y directions and on the z direction the expansion is from 2.55 Å to 2.65 Å. For copper, this expansion means that it lacks the bonds that it would naturally have in the bulk and therefore it will become less stable. The result is clearly seen in the shift of the d-band center towards the Fermi level. As shown in Figure 55, the d-band center shifted from -2.55 eV in a Cu(111) to -1.94 eV in the Au(111) slab with the replaced copper top layer.

The Cu bilayer on Au(111) model can help discern between the ligand effects and the geometric effects that change the d-band shape and alter the reactivity of core/shell alloys. As expected, Cu top layer on the Cu bilayer Au(111), undergoes a compression on the z direction, in fact, it contracts as compared to the Cu(111) top layer. This contraction from 2.55 Å to 2.47 Å can be explained because of the expansion that copper is undergoing on the xy plane. Due to the expansion from 2.57 Å to 2.95 Å, the top layer of copper will bond strongly to the underlying layer as was previously, seen on the PdAu core-shell models. As shown in Figure 55, this first layer has a d-band shift from -2.55 eV to -1.97 eV which is very similar to the shift of the Cu monolayer on Au(111) case but now there coordination to all Cu atoms instead of Au. It is plausible that change in the identity of the metal in the underlying layer and the compression
of the geometry have opposing effects on the shape of the $d$-band center. In fact by fixing the 
Cu monolayer on Au(111) geometry and changing the nature of all atoms to Cu, it is possible to 
isolate the geometric effect. For this case, the shift of the top layer is to -1.85 eV, even further 
than that of the Cu monolayer on Au(111) which clearly indicates that geometric effects will 
push the $d$-band center even closer towards the Fermi edge. This result translates in the 
corrobration that orbital extent and geometric effects have counteracting effects on the 
position of the $d$-band. Lattice expansion drives the $d$-band towards the Fermi edge whereas 
the differences orbital extent actually moves the center of the $d$-band to lower energy.

The second layer of copper on the Cu bilayer Au(111) model is in expansion in all three 
directions (2.70 Å on z and 2.95 on xy plane). Compared to the copper of the Cu monolayer on 
Au(111) difference with the Cu(111), the expansion on the z direction of the second layer of the 
bilayer Cu on Au(111) is over double of the monolayer case (0.166 Å difference between 
Cu(111) and Cu bilayer on Au(111)). The expansion combined with the coordination to gold, has 
the effect of shifting the $d$-band center towards higher energy (Cu(111) second layer -2.66 eV to 
Cu bilayer Au(111) second layer -2.12 eV). For this layer there are two effects that can alter the 
$d$-band center, the geometry, and overlap of $d$-orbital. Previous discussion on monolayer cases 
of Cu on Au, it was shown that geometric effect would drive the center towards the Fermi level 
and an opposite effect would be seen due to orbital overlap. The change on the monolayer $d$-
band shift is of 0.61 eV whereas for the second layer of the bilayer model is 0.54 eV. This 
decrease in the amount of the shift can be attributed to the increase in the coordination 
number which is actually stabilizing the layer and thus has the same direction as the orbital 
extent.
Figure 55 Density of states profile for the surface layer of Cu(111) and a monolayer of Cu above Au(111).

Figure 56 Density of states profile for the surface layer of Cu(111) and first layer a bilayer Cu shell above Au(111) (left). PDOS of the second layer of Cu(111) and second layer of a bilayer shell of Cu above Au(111).
When the structure is reversed and a single layer of Au is placed above Cu(111) the monolayer of gold is compressed from 2.95 Å to 2.57 Å in the xy plane and to 2.87 Å in the z direction. This extreme compression is seen in the significant shift of the gold’s $d$-band center away from the Fermi level from -3.41 eV to -4.13 eV as shown on Figure 57. However, in the case of a Au bilayer above Cu(111), the first layer of gold pushes away from the slab to an unrealistic distance metal-metal bond distance of 3.63 Å. Therefore, this structure is deemed to be unstable. It is possible to perform a calculation of a constrained bilayer of Au above Cu(111) by fixing the positions of all atoms. For this model, the $d$-band center actually is shifted even further from the Fermi edge to -4.29 eV.

![Figure 57 Density of states profile for the surface layer of Au(111) and a monolayer of Au above Cu(111).](image-url)
4.4 Conclusions

The combination of effects present in core-shell alloys is more complex than for homogeneous alloy particles. Lattice strain effects in both the xy plane and in the z direction may be present, sometimes acting in opposite manner. In addition, differences in orbital extent between elements may result in shifts in the d-band centers of the alloys.

Further work should be done to understand how different surface planes would influence the changes in the XANES. A step towards this goal of approximating the experimental set up is the core-shell model of a Au$_{55}$ cluster, in which the external layer of gold is replaced by Pd. Preliminary results on a monolayer coverage on Au in a icosahedral 55 atom particle show the contraction of the Pd-Pd bond to 2.76 Å as compared to the Pd(111) distance of 2.80 Å (z direction) and 2.79 Å (xy plane). Similar contraction is seen on the bond of the Pd layer to the Au sublayer (2.77 Å) while in the Pd monolayer on Au(111) model, the distance from first to second layer is 2.84 Å. A intermediate upshift in the $d$-band is seen on the Pd monolayer of the 55 atom cluster (-1.49 eV) that resides in between the $d$-band positions of the Pd monolayer on Au(111) (-1.64 eV) and the Pd(111) top layer (-1.29 eV). Although computationally expensive, a more realistic model could include partial segregation of one of the metals to the shell as well as coverages less than a monolayer.
5 CO ADSORPTION ON Pd-Pt BIMETALLIC SURFACES

5.1 Introduction

A key question that emerges in alloy nanoparticle catalysis is how the bulk composition and the surface composition are interrelated. Segregation of one metal vs. another often results as the particle seeks to minimize its free energy. Obtaining quantitative information about the surface composition is a challenging task whereby a combination of experimental and computational characterization must be applied to give insight of the composition and morphology of bimetallic nanoparticles. Two very powerful characterization tools can be correlated to provide the surface composition: Infrared spectroscopy and X-ray absorption spectroscopy. This type of characterization has been demonstrated by Wu et al. to provide information regarding the surface composition of catalyst composed by Pd-Pt with the use of CO adsorption, DRIFTS and XAS. In this thesis chapter we will describe the experimental strategy applied by Wu et al. and the use of density functional theory calculations which aided in the interpretation of the experimental results.

Traditionally, turnover rates for supported metal nanoparticles can be determined by using chemisorption or infrared techniques but the problem arises when both metals in the bimetallic adsorb the molecule used and therefore it becomes difficult to determine the surface composition of the catalyst and the site density of the surface. Wu et al. proposed a method of
combining IR and XAS to provide an insight into the composition of the surface while studying neopentane isomerization and hydrogenolysis as a test reaction (57). Neopentane conversion has two main paths: isomerization and hydrogenolysis. While isomerization results in the formation of isopentane or even n-pentane which serve as model reactions for hydrocarbon reforming, hydrogenolysis results in the production of unwanted methane and isobutane (with further decomposition to smaller alkanes and methane in subsequent steps). The study used four catalysts: Pd, Pt, and two PdPt with nominal compositions of 1% Pd 2% Pt and 0.75%Pd 3%Pt, all supported on SiO$_2$. To briefly summarize, Pt (64 %) was found to be much more selective to isomerization than Pd (5 %). In addition, turnover rates of neopentane conversion were shown to be higher on the pure Pt catalyst and the pure Pd one than in both bimetallic catalysts. Comparing to the highest bimetallic turnover rate, Pt has double the TOR of the 0.75%Pd + 3% Pt and Pd has 12% higher TOR than the same bimetallic, showing that the activity of the catalysts is perturbed by alloying. Also, selectivity was shown to increase to approximately 70% in the bimetallic (even higher than Pt) which shows a synergistic effect upon alloying since the properties of the new catalysts are not an average of those of the pure metals. The presence of Pd and Pt in the nanoparticles of the bimetallic catalysts was confirmed by using EDX and the formation of a PdPt alloy was also confirmed by XAS measurements.

The presence of adsorbates on the surface of metallic nanoparticles has been shown to modify the intensity of the leading absorption edge of the metal (170). By using $\Delta$XANES (subtraction of XANES in He from that of CO adsorbed on the sample) one can isolate the effect of the adsorbate and correlate the $\Delta$XANES with the adsorbate coverage (57). Due to the fact that XAS is element specific, the change in both edges, Pd and Pt, due to the presence of CO can
be measured. By making a series of assumptions about the relationship between surface geometry and CO coverage (informed by the IR spectra), from the ΔXANES, Wu et al. made estimates for the surface fractions of the metals in the bimetallic nanoparticles. For example, for 1%Pd-2%Pt bimetallic catalyst the ΔXANES measurements correlate to a surface composition of 68% Pt and 32% Pd. The method proposed by Wu et al. is viable as long as the saturation coverage is achieved, there is no restructuring of the particle upon adsorption of the test molecule (as compared to the reactive environment), and the particle size is lower than 10 nm. Density functional theory calculations of adsorption behavior of CO on the pure and bimetallic model as well as density of states profiles, help explain the role of Pd on the bimetallic catalyst in which the Pt d-PDOS shows electronic alteration of the Pt in the bimetallic making it more reactive and thus changing the energy of adsorption of the CO molecule.

CO adsorption has been well studied on many single crystal metal surfaces and it is widely known that CO adsorbs in an orderly manner on palladium and platinum surfaces. With this previous knowledge, we can now envision a characterization of a bimetallic surface by using the predetermined CO adsorption order. Previous studies of CO adsorption on Pt(111) surfaces show that the preferred adsorption site changes as the surface coverage increases (171) (172) (173). At a low adsorption coverage of 0.25 ML, CO adsorbs on atop sites (174) (171). An increase in coverage to 0.33 ML, changes the preferred adsorption site to fcc trifold hollow site with a lattice of (v3xv3R30°) (175). It has been noted by various authors that increase from 0.33 ML to 0.5 ML coverage has a transition from hollow site adsorption to bridge sites and atop sites (173) (171) (176) and a further increase in coverage to 0.6 ML creates a transition to a mixture of bridge and hcp hollow sites (177) (171). Finally, saturation coverage of
0.75 reverts to atop site adsorption (178). A similar trend is found for Pd(111), where the coverage lattice changes as the amount of CO adsorbed on the surface increases. Pd(111) starts with a hollow site configuration for low coverage and transitions to bridge and hollow site (179) (180) (173). Finally, at saturation coverage, a combination of atop and trifold hollow site is seen (179) (181). Studies on CO adsorption on PdPt alloys are not as abundant as adsorption on pure Pd or pure Pt. Previously Yu et al. proposed a similar method to that by Wu et al. in which the surface composition was being determined based on CO adsorption IR data. Through a combination of NMR, CO adsorption IR, TEM and XANES Yu et al. examined four PdPt catalysts supported on amorphous silica-alumina and silica, (182). Using TEM, the bimetallic nanoparticles were estimated to have particle sizes ranging from 1.4 to 1.8 nm. Coordination numbers obtained from the fitting of the Pt L_{III} and Pd K edges of the EXAFS showed that Pt had a higher coordination number than Pd, (CN_{Pt} = 11 and CN_{Pd} =6). The results suggest that the Pt is primarily located in the bulk whereas the Pd is located primarily at the surface and thus the particles have a core-shell structure with a Pd rich shell. For the determination of the surface composition, Yu et al. used infrared spectroscopy of CO adsorption on the bimetallic (in which a scan was taken) followed by evacuation of the chamber containing the catalyst (at this point a second scan was taken). According to Yu et al, subtraction of the evacuated scan from the initial scan with CO leaves only the CO adsorbed onto Pt atoms. A control experiment in which CO IR was taken after CO dosing and after evacuation shows that CO is completely desorbed from Pd therefore confirming that the CO left after evacuation on the PdPt alloy is most likely the one adsorbed on Pt. For PdPt/SiO_{2} the peak at 2095 cm^{-1} was assigned to CO atop site of the overlap of both Pd adsorbed CO and Pt adsorbed CO. After evacuation, the peak for linear CO shifted to
2074 cm\(^{-1}\), thus deconvolution of the atop adsorption peaks yielded that this peak is assigned to Pt adsorbed CO. Bridge bonded CO on Pd was observed under 2000 cm\(^{-1}\) and a lower band between 1860 cm\(^{-1}\) and 1920 cm\(^{-1}\) was assigned to a complex Pd\(_2\)CO. Using the intensity of the IR peaks before and after evacuation, a quantification of the surface composition was determined in which Pt atoms were present on the surface in the range of 13.9\% - 16.9\% for all four samples. The XANES data also reflect enrichment of Pd at the surface. It was hypothesized that the adsorption of Pt atoms is affected by the support used, because the Pt surface fraction increased on supports with high ratios of alumina (182).

Other studies have focused on qualitative interpretation of the surface composition based on CO adsorption on PdPt bimetallics. D’Souza and Sampath used chemisorption of CO as means of characterizing the surface composition of PdPt nanoparticles stabilized with a sol-gel matrix (183). Comparison of the IR spectra of the bimetallic with a physical mixture of pure Pd and pure Pt particles with the same Pd:Pt ratio showed differences confirming the formation of an alloy. Atop adsorption of CO was seen at 2030 cm\(^{-1}\), 2036 cm\(^{-1}\), and 2037 cm\(^{-1}\) for Pd, Pt and PdPt respectively. The band observed at 2037 cm\(^{-1}\) suggests the formation of a core-shell alloy with a Pt rich shell. This core-shell structure is observed for different ratios of Pd:Pt in which Pt is present mainly on the shell. However, when the ratio of Pd:Pt rises to 0.75:0.25, both metals coexist on the surface due to the lack of Pt to cover the Pd core, and this is reflected by the atop band observed at 2026 cm\(^{-1}\) and a strong bridge band at 1961 cm\(^{-1}\). The core-shell structure was confirmed with XPS by etching a thick film of the catalysts and taking scans at regular time intervals. After 35 min etching, Pd peaks start showing on the XPS, though scans at shorter times revealed only Pt (183). Nilekar et al. also showed formation of a core-shell
structure using IR spectroscopy by examining CO adsorption on bimetallic catalysts as a function of Pt concentration. In this study, a Pt rich shell and Pd rich core was reported. Formation of the core-shell structure is seen by the blue shift and increase in intensity of the atop CO adsorbed on Pt as the amount of Pt is being added to the sample (184). Carbon monoxide adsorption on PdPt has also been used to determine dispersion by assuming the stoichiometry of CO to Pd or Pt to be unity (185) (186). The decrease in the Pd CO bridge band is attributed to the formation of the core shell alloy, as fewer Pd-Pd sites are observed which would allow for bridge bonding CO. CO FTIR has also been used to determine adsorption sites on the surface, being the bands assigned to atop (2067 cm⁻¹), hollow site (1866 cm⁻¹) for PdPt (187). In this work, we will discuss DFT calculations performed in support of the experimental studies of Wu et al (and the others mentioned above). Specifically we will examine the effect of CO coverage and surface composition on the predicted IR C-O stretching frequencies. We will also use DFT to attempt to explain the observed changes in reactivity of the surface via density of states calculations.

5.2 Methodology

In order to predict surface composition using computational models, a comparison between well studied experimental CO adsorption vibrational spectroscopy and calculated vibrational modes is performed. As a gross approximation, low Miller index planes have been used to model the nanoparticles. A proposed mixture between the adsorption patterns on Pd(111) and Pt(111) is proposed for the PdPt(111) surface for the different coverages of 0.25, 0.33, 0.5, 0.6 and 0.75 ML and are shown in Figure 58. To carry the simulation of the different
surfaces, Vienna Ab-Initio Simulation Package (VASP) was used (40) (39). Calculations of the (111) surfaces were carried using a plane-wave basis set with a cutoff energy of 400 eV and projected augmented wave pseudopotentials (47) (48). The Perdew-Burke-Ernzerhof (PBE-GGA) form of the correlation and exchange energy was used in all calculations (52) (51). In order to create the PdPt(111) surface, a bulk fcc structure was used with Pd atoms and Pt atoms present in a 1:1 ratio. A starting bond distance of the average of the monometallic bulk structures was used and allowed to relax for optimization. Once the bulk structure was optimized, a (111) plane was cleaved with six layers. On all surfaces, the bottom two layers were fixed to mimic bulk properties and the remaining layers were left to relax. Vacuum space of approximately 4 layers was set in the z direction to prevent spurious interactions between slabs. A Monkhorst Pack kpoint grid of 5x5x1 was used on all 2x2 unit cell calculations (81).

At 0.25 ML coverage, CO was adsorbed on different sites: atop, bridge, 3-fold hollow hcp, and 3-fold hollow fcc.
Figure 58 CO adsorption on PdPt(111), Pd (blue), Pt (green), C (grey), O (red). Left Column: 0.25 ML, 0.33 ML, 0.50 ML. Right column: 0.60 ML, 0.66 ML, 0.75 ML.

Following experimentally and computational suggested adsorption structures for CO on Pd and Pt, a (2x3) rect (171), (V3x3)R30° (171), (V3x2) rect (173), and (V3x2) (172) patterns were calculated for adsorption of coverages of 0.25, 0.33, 0.5, 0.6, and 0.75 respectively on
Pt(111) shown in Figure 59. For Pd(111) a $c(4\times2)$-1 (180), $(\sqrt{3}\times\sqrt{3})R30^\circ$ (179), $c(4\times2)$-2 (179), $c(\sqrt{3}\times5)$ rect (173), and a $(2\times2)$ (179) structures were optimized and are portrayed in Figure 60. Reported energies are normalized per CO molecule adsorbed.

Figure 59 CO adsorption on Pt(111). Left column: 0.25 ML, 0.33 ML. Center: 0.50 ML. Right column: 0.60 ML, 0.75 ML
VASP calculates vibrational frequencies by diagonalization of the Hessian matrix created from the numerical second derivative of the energy with respect to each Cartesian coordinate. Vibrational frequencies were scaled according to a scaling factor generated by calculation of gas phase CO $2103 \text{ cm}^{-1}$ by DFT vs. $2143 \text{ cm}^{-1}$ from experiments (18)). Simulation of vibrational frequencies was carried out by holding the six layers of the surface frozen and allowing only the CO molecules to move.

Density of states profiles were calculated using CASTEP (189). Single point calculations were run with PBE-GGA pseudopotentials and 400 eV cutoff energy. For calculations of the density of states profiles and EELS, the same Monkhurst Pack kpoint grid parameters were used as the VASP optimization.
Figure 60 CO adsorbed on Pd(111). Left column: 0.25 ML, 0.33 ML, 0.50 ML. Right column: 0.6 ML, 0.6 ML fixed structure, 0.75 ML.

5.3 **Results**

The projected density of states for Pd(111) vs. Pd in PdPt(111) as well as Pt(111) vs. Pt in PdPt(111) are compared in Figure 61. From the Figure one can see that the Pt d-band width
decreases in alloy relative to Pt(111) whereas the Pd d-band width increases in the alloy as compared to Pd(111). The d-band centers of the top layer are affected by this change in width since the degree of filling for Pt and Pd changes only minimally when alloyed. We find that the d-band center for Pd shifts away from Fermi level (Pd(111) Ed = -1.76 eV; Pd in PdPt(111) Ed = -1.84 eV) when alloyed with Pt. Conversely, the d-band center of Pt shifts toward the Fermi level (Pt(111) Ed = -2.15 eV; Pt in PdPt(111) Ed = -2.05 eV).

Figure 61 Projected density of states. Left: Pt(111) (green) vs. Pt in PtPd(111) (black). Right: Pd(111) (blue) vs. Pd in PtPd(111) (black).
Tables VIII though X have a compilation of the adsorption energies and vibration frequencies found with VASP for Pt(111), Pd(111), and PdPt(111). CO molecules were adsorbed onto Pd(111) at a coverage of 0.25 ML and it was found that CO adsorbed preferentially on hollow sites (fcc, hcp -2.05 eV) followed by bridge sites (-1.91 eV) and finally atop (-1.50 eV) being the least favorable adsorption site for this coverage in agreement with experiment. On the Pt(111) surface, adsorption energies between sites only vary in a range of 0.24 eV being the most favorable the fcc and hcp 3-fold hollow sites with -1.91 eV and -1.94 eV respectively. Following the 3-fold hollow sites is the Pt-Pt bridge site with -1.88 eV and finally atop with an adsorption energy of -1.70 eV. Experimentally, Pt(111) CO adsorption at a 0.25 ML coverage has a preferred site on atop. The difference in preferred adsorption site at this coverage comes from the preference towards overcoordination within DFT (190). Vibrational frequency calculated for the atop site of the 0.25ML coverage structure on Pt(111) averaged 2084 cm\(^{-1}\), which is in good agreement with the experimental value of 2092 cm\(^{-1}\) reported by Roeterdink et al. (174) being able to reproduce experimental data, now we can move forward to higher coverage.
Table VIII Energy of adsorption and vibrational frequency of CO on Pt(111)

<table>
<thead>
<tr>
<th>Coverage (ML)</th>
<th>Eads (eV)</th>
<th>Vibrational Frequency (cm(^{-1}))</th>
<th>Adsorption Sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>-1.70</td>
<td>2084</td>
<td>atop</td>
</tr>
<tr>
<td>0.33</td>
<td>-1.63</td>
<td>2082</td>
<td>atop</td>
</tr>
<tr>
<td>0.5</td>
<td>-1.56</td>
<td>2108</td>
<td>atop</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1867</td>
<td>Bridge</td>
</tr>
<tr>
<td>0.6</td>
<td>-1.47</td>
<td>2112</td>
<td>atop</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1821</td>
<td>hcp 3-fold hollow site</td>
</tr>
<tr>
<td>0.75</td>
<td>-1.03</td>
<td>2064</td>
<td>atop</td>
</tr>
</tbody>
</table>

Focusing on the Pt(111) surface, an increase to 0.33 ML has a decrease in energy of adsorption per CO molecule from -1.70 eV for the 0.25 ML to -1.63 eV. The preferred adsorption site for this coverage is still atop sites with a vibrational frequency average of 2082 cm\(^{-1}\). At 0.5 ML the structure transitions to a combination of atop and bridge sites with vibration frequencies of 2108 cm\(^{-1}\) and 1867 cm\(^{-1}\) respectively. Compared to the experimental data reported by Tushaus et al. there is reasonable agreement between the calculated vibrational frequency of the atop site and the experimental one (2104 cm\(^{-1}\)) as well as on the bridge site where the experimental data is 1854 cm\(^{-1}\). Based on the structure proposed by Yakovkin et al. for the 0.6 ML coverage, a combination of atop and hcp 3-fold hollow sites was optimized and average vibrational frequencies of 2112 cm\(^{-1}\) and 1821 cm\(^{-1}\) were found. Experimentally, a saturation coverage of approximately 0.67 ML of CO on Pt(111) has been reported (177) although Rodes et al. reported a coverage of 0.75 ML by using electrochemical IRAS measurements on Pt(111) electrodes (178). For 0.75 ML a vibration frequency of 2064 cm\(^{-1}\).
was calculated which matches with the experimental value of 2070 cm$^{-1}$. Structures built have been now validated by comparison with experimental data available.

Table IX Energy of adsorption and vibrational frequency of CO on Pd(111)

<table>
<thead>
<tr>
<th>Coverage (ML)</th>
<th>Eads (eV)</th>
<th>Vibrational Frequency (cm$^{-1}$)</th>
<th>Adsorption Sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>-2.05</td>
<td>1826</td>
<td>fcc 3-fold hollow site</td>
</tr>
<tr>
<td>0.33</td>
<td>-1.93</td>
<td>1819</td>
<td>fcc 3-fold hollow site</td>
</tr>
<tr>
<td>0.5</td>
<td>-1.89</td>
<td>1916</td>
<td>fcc 3-fold hollow site</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1840</td>
<td>hcp 3-fold hollow site</td>
</tr>
<tr>
<td>0.6</td>
<td>-1.34</td>
<td>2071</td>
<td>atop</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1874</td>
<td>bridge</td>
</tr>
<tr>
<td>0.75</td>
<td>-1.59</td>
<td>2114</td>
<td>atop</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1898</td>
<td>fcc 3-fold hollow site</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1827</td>
<td>hcp 3-fold hollow site</td>
</tr>
</tbody>
</table>

On pure Pd(111), at a surface coverage of 0.25 ML a calculated vibrational frequency of 1826 cm$^{-1}$ was found for fcc 3-fold hollow sites which is in agreement with the experimental value of 1833 cm$^{-1}$ (191). Increase in coverage to 0.33 ML also has a decrease in energy of adsorption, as in the case of Pt(111), from -2.05 eV to -1.93 eV. Transition from an fcc 3-fold hollow site to a combination of hcp and fcc 3-fold hollow site, is seen at a 0.5 ML. At this
coverage, the fcc vibrational frequency is 1916 cm\(^{-1}\) and for hcp 1840 cm\(^{-1}\). Hoffmann et al. reported a 3-fold hollow site vibration of 1936 cm\(^{-1}\) for the 0.5 ML coverage and for the 0.6 ML atop and bridge sites had frequencies of 2097 cm\(^{-1}\) and 1893 cm\(^{-1}\) respectively (179) per reference (192). Since only bridge and atop adsorption is observed at the high coverages achieved in the experiments of Wu et al, a coverage of 0.6 ML was simulated by fixing the CO molecules on atop and bridge positions in the x and y directions and allowing them to move only in the z direction due to DFT’s tendency to overcoordinate and shift the adsorption site to 3-fold hollow sites. Vibrations of 2071 cm\(^{-1}\) and 1874 cm\(^{-1}\) for atop and bridge sites were obtained. The discrepancy between the experimental bridge site and the computational one could be related to the restriction of movement of the molecules in the xy plane. Saturation coverage of 0.75 ML was simulated with a combination of atop, fcc and hcp 3-fold hollow sites. In comparison with Tushaus et al. reported frequencies, the atop is only 4 cm\(^{-1}\) more than the experimental and the 3-fold hollow site reported is 1894 cm\(^{-1}\) (173) which is similar to the fcc 3-fold hollow site calculated at 1898 cm\(^{-1}\), though no distinction of fcc or hcp hollow site can easily be made from the experimental data.
In order to examine the surface of a Pd-Pt alloy, a bulk of PdPt was optimized and a (111) surface with 50% Pd and 50% Pt was chosen to represent an alloy nanoparticle. A series of coverage structures were calculated and at the lowest coverage of 0.25 ML a vibrational frequency of 1801 cm\(^{-1}\) and an adsorption energy of -2.14 eV was found. Compared to the pure metal counterparts, the adsorption on the hcp trifold hollow site is slightly more favorable than that of a Pd(111) 3-fold hollow site by 0.1 eV which is partially due to the presence of Pt on the surface. For this structure the CO molecule is adsorbed to a 3-fold hollow site composed of two

<table>
<thead>
<tr>
<th>Coverage (ML)</th>
<th>Eads (eV)</th>
<th>Vibrational Frequency (cm(^{-1}))</th>
<th>Adsorption Sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
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<td>hcp 3-fold hollow site</td>
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<td>-1.84</td>
<td>1819</td>
<td>fcc 3-fold hollow site</td>
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<td>0.5</td>
<td>-1.76</td>
<td>1922</td>
<td>PtPt bridge</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1876</td>
<td>PdPt bridge</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1858</td>
<td>fcc 3-fold hollow site</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1831</td>
<td>Pt hcp 3-fold hollow site</td>
</tr>
<tr>
<td>0.6</td>
<td>-1.74</td>
<td>2073</td>
<td>Pt atop</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1884</td>
<td>PtPd bridge</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1800</td>
<td>fcc 3-fold hollow site</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1789</td>
<td>Pd hcp 3-fold hollow site</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1780</td>
<td>Pt hcp 3-fold hollow site</td>
</tr>
<tr>
<td>0.66</td>
<td>-1.17</td>
<td>2092</td>
<td>Pd atop</td>
</tr>
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</tr>
<tr>
<td></td>
<td></td>
<td>1865</td>
<td>PdPd bridge</td>
</tr>
<tr>
<td>0.75</td>
<td>-1.36</td>
<td>2103</td>
<td>Pt atop</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1872</td>
<td>Pt hcp 3-fold hollow site</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1806</td>
<td>fcc 3-fold hollow site</td>
</tr>
</tbody>
</table>
Pt atoms and one Pd. With an increase in coverage to 0.33 ML, the adsorption energy now behaves as an intermediate between that of Pt(111) and Pd(111). This structure resembles that of Pd(111) with fcc 3-fold hollow sites and an average vibration frequency of 1820 cm\(^{-1}\). This structure has an even number of Pd atoms and Pt atoms in contact with the CO molecules, thus the intermediate behavior of the energy of adsorption. The same trend is seen on the 0.5 ML coverage where there is a combination of bridge sites, fcc 3-fold hollow sites, and hcp 3-fold hollow sites and the energy of adsorption on the alloy is -1.76 eV per CO molecule while on Pd(111) the energy of adsorption is -1.89 eV and on Pt(111) -1.56 eV. The structure for 0.6 ML has all the adsorption sites of Pd(111) and Pt(111) combined. Comparing the bridge sites on the alloy and the Pd(111), there is a decrease in the frequency from 1956 cm\(^{-1}\) to 1884 cm\(^{-1}\) upon alloying due to the involvement of a Pt atom in the bonding of CO to the surface. At 0.6 ML coverage the energy of adsorption per CO molecule is closer to that of the Pd(111), but in this case the alloy has a slightly higher energy of adsorption than that of the pure Pd slab.

For comparison purposes, a 0.75 ML coverage was carried on all surfaces since experiments performed by Wu et al. were carried in a manner that the saturation coverage is expected. Vibrational frequencies for the Pd(111), PdPt(111), and Pt(111) were calculated at 2114 cm\(^{-1}\), 2103 cm\(^{-1}\), and 2064 cm\(^{-1}\) for Pd atop, Pt atop, and Pt atop respectively. Although the frequencies are systematically higher than those observed experimentally (2082, 2073, and 2071 cm\(^{-1}\) respectively), the DFT calculated frequencies do follow the same trend with regard to the order. Furthermore, experimentally two peaks are observed on the Pt nanoparticle, one located at 2071 cm\(^{-1}\) and a broader one at 1810 cm\(^{-1}\) that were assigned to atop and bridge sites. Comparison with the proposed model for Pt(111) there is only a shift of 7 cm\(^{-1}\) which
suggests that the saturation coverage was achieved and a prevalence of atop adsorption sites on a (111) faceted particle is reasonable model

As mentioned before, Pt(111) saturates at a CO coverage of 0.63 ML. At a CO coverage of 0.6 ML Avery reports the presence of bridge sites that resemble the hcp 3-fold hollow sites of the 0.6 ML model. For both the 0.6 and 0.5 ML coverages on Pt(111), the bridge site vibrational frequencies are in better agreement with the calculated rather than the lower frequency of 1810 cm\(^{-1}\) reported by Wu et al. This result seems to suggest that the nanoparticles present in this study possess surfaces other than just (111) facets. For Pd nanoparticles, a vibration frequency of 2082 cm\(^{-1}\) for atop site and 1945 cm\(^{-1}\) for bridge site was reported experimentally. Again, a model of a (111) surface was used. A saturation coverage involving a combination of 3-fold hollow sites and atop sites was chosen as a computational model. The atop vibration was 2114 cm\(^{-1}\) whereas the fcc 3-fold hollow site was 1898 cm\(^{-1}\) and the hcp 1827 cm\(^{-1}\). Tushaus et al. report obtaining a vibrational frequency of 2110 cm\(^{-1}\) for the atop site on Pd(111) at a 0.75 ML coverage and 1894 cm\(^{-1}\) for the 3-fold hollow sites. Comparing the FTIR data from Wu et al. to the proposed model it is clear that there is disagreement in the assignment of the low frequency peak such that one must conclude that no 3-fold hollow site CO adsorption occurs. Instead, CO adsorbs to bridge sites that are not predicted for the Pd(111) saturation models. One possibility is that sites exist on the nanoparticle that are similar to the 0.63 ML coverage of CO. At that coverage, Guo and Yates show the presence of a mixture of bridging and atop sites in a Pd(111) domain of 8x4√3 structure with frequencies of 1951 and 2097 cm\(^{-1}\) which are in good agreement with the experimental results reported by Wu. We have approximated this structure by generating a (V3×V7)R30 structure which contains 4 atop sites and 2 bridge sites
(note that the CO molecules were fixed to these sites by freezing their motion in the x-y plane due to their preference for 3-fold hollow site adsorption at this coverage on Pd(111), as a consequence of overcoordination preferred by DFT). We have calculated the vibrational frequencies of CO in this structure to be at approximately 1863 cm\(^{-1}\) for the bridge sites (again a significantly lower frequency than the experimentally observed value of 1945 cm\(^{-1}\)) and 2071 cm\(^{-1}\) for the atop sites. Another explanation is that the bridge sites arise on different facets. Therefore, we have also examined a Pd(110) surface with coverages of 0.5 and 0.75 ML. Bridge sites on Pd(110) have a calculated vibrational frequency averaging 1916 cm\(^{-1}\) for the 0.5 ML coverage, suggesting the possibility of sites akin to the a (110) plane to be present in the Pd nanocluster.

Adsorption of CO on the PdPt alloy was carried using a combination of the coverage structures mentioned above. CO adsorption on the PdPt(111) surface at 0.6 ML shows features which are nominally consistent with the frequencies reported in the alloy nanoparticle characterized by Wu et al. with atop adsorption peak at 2073 cm\(^{-1}\) and a dim broad bridging peak at 1900 cm\(^{-1}\). The structure proposed for the 0.6 ML adsorption on PdPt(111) is a combination of atop, bridge, and trifold hollow sites with calculated vibrational frequencies of 2073 cm\(^{-1}\), 1884 cm\(^{-1}\), 1790 cm\(^{-1}\), on average respectively. Of course, while the calculated surface structure possesses only PdPt bridge sites, the nanoparticles likely possess both Pt-Pt and Pd-Pd in addition to Pd-Pt sites and therefore shows a broad feature. As demonstrated in our simple examination of adsorption at atop sites in the alloy in Table X, the frequencies of the atop Pd and Pt converge in the alloy leading to the experimentally demonstrated result shown in Figure 62 replicated from Wu et al., whereby the frequencies of CO adsorption at atop sites
in the alloy are intermediate to the monometallic catalysts. At saturation coverage, the CO Pt atop has a vibrational frequency of 2103 cm\(^{-1}\) which is at a 1.6% error from the experimental data reported. A 0.66 ML structure was created to reflect the adsorption sites of the experimental data and the preference of the PdPt to adsorb on atop sites. Adsorption energies decrease dramatically as the coverage increases. For example, as the coverage goes from 0.6 ML to 0.66 ML coverage, the CO adsorption energy decreases by 0.16 eV per CO molecule and further increasing the coverage to 0.75 ML the CO adsorption energy further decreased by 0.22 eV per CO molecule.
Figure 62 DRIFTS CO adsorption on Pt, PdPt, and Pd supported on SiO$_2$ reproduced from (57).

5.4 Discussion

The position of the $d$-band with respect to the Fermi level has been widely used as a descriptor of catalytic performance (6) (3) (4). The shifts observed on the density of state profile show Pd shifting away from the Fermi edge, translating into less reactivity of the Pd atoms in the alloy model. The opposite happens for Pt where the shift of the alloy’s $d$-band is towards the Fermi edge, thus increasing Pt atoms reactivity upon alloying. This trend of decreased and increased reactivity by Pd and Pt is also seen in the CO adsorption energy. It would follow that
the expansion of Pd by Pt would account for this behavior since the Pt lattice is larger than that of Pd, however this situation would correspond to a narrowing of the Pd PDOS and conversely an expansion of the d-band of Pt, which is not the situation observed. The actual behavior is explained by the orbital extent of Pd and Pt. Due to larger orbital extent of Pt as compared to that of Pd (115), there is a greater overlap of the d orbital of Pd with Pt, thus resulting in a feeling of “overbonding” from Pd. The lack of the overlap of Pt with neighboring Pd, brings an opposite effect on Pt which now feels “underbonded” by the presence of Pd. A physical manifestation of the difference in orbital extent are seen in the great difference in melting temperature of Pt (1768 °C) and Pd (1555 °C) (193).

In order to simplify the effect of alloying, we have also examined the adsorption of CO on the three surfaces in the atop configuration at 0.25 ML. When comparing only CO atop adsorption on the three surfaces, the adsorption energy on Pt (-1.7 eV) is higher than on Pd (-1.5 eV). An enhanced behavior is seen on the alloy, which adsorbs CO stronger on Pt atop (-1.90 eV) than pure Pt and weaker on Pd atop (-1.39 eV) than the pure Pd. As we alloy Pt with Pd, the CO adsorption energy of Pd decreases; while the CO adsorption energy of Pt increases. The adsorption behavior observed here falls outside the range defined by the pure metals and therefore alloying leads to new unexpected behavior which would not be predicted by averaging the characteristics of the two metals. This type of behavior by alloying has been reported on other alloys such as PdCu (13) and explained as a consequence of electronic effects resulting from lattice strain and ligand effects. Although the d-band center for Pd is closer to the Fermi level than that of Pt and therefore has a higher heat of adsorption than Pt, this is not true for atop adsorption of CO, since CO actually prefers the 3-fold hollow site on Pd (179).
However, this model is a simple demonstration which shows that upon alloy formation with Pt, Pd chemisorbs CO with a lower heat of adsorption than monometallic Pd. Calculations on other sites (bridge, fcc) show similar trends, thus is not limited to atop coordination. Both the DFT calculations of CO adsorption and our catalytic turnover rates and selectivity for neo-pentane hydrogenolysis/isomerization suggest that the bimetallic PtPd catalysts are unique and display behavior different from those of the monometallic catalysts. This behavior has been predicted for other alloy systems due to synergistic combinations of strain and ligand effects (13). If the alloy catalyst possessed behavior that was simply an additive behavior of its two parts, then we would expect that the activity of the catalyst would lie between Pt and Pd and that the selectivity would also lie between Pt and Pd. Instead Wu et al. have observed that both the activity and selectivity lie outside of the range defined by the monometallic catalysts (57). It appears that neo-pentane conversion has been significantly turned off on Pd surface sites, which predominately yield hydrogenolysis. Like CO, it appears that perhaps neo-pentane adsorption (and activation) is weakened on Pd sites in the alloy. We can further speculate from the IR data that few hollow or bridging Pd sites exist in the alloy surface. This implies that an additional effect of alloying is the disruption of these sites where the molecule can experience high coordination with surface Pd which lead to hydrogenolysis (194). In contrast, adsorption of neo-pentane to active sites on Pt may follow the example of CO adsorption where atop sites are desirable (195).
5.5 **Conclusions**

Use of density functional theory based calculation can potentially aid in characterizing the surface composition of bimetallics in which both metals have similar adsorption pattern. Validation of the application of the Hammer and Norskov $d$-band method was proven by observing the shifts in the center of the $d$-band and the adsorption energy of CO on the different surfaces. The synergistic property of the bimetallic on the selectivity towards isomerization on the neopentane hydrogenolysis could be related to the strength of adsorption of CO onto the surface. In order to accurately determine the surface composition of a single metal cluster or bimetallic, a broader library with different adsorption coverages on a wide variety of surface planes is needed. In addition, experimental results reported in the introduction suggest that synthesized particles with core-shell structures as well as decorated surfaces with different surface compositions can be created. The possibility for different types of structures implies that the proper descriptive models are potentially more complex than we have imagined here depending on the percentages of Pd or Pt present on the surface, thus requiring the suggested library to also include different surface ensembles as well as core-shell alloys.
6 DENSITY FUNCTIONAL THEORY STUDY OF THE SELECTIVE HYDROGENATION OF ACROLEIN ON SILVER AND SILVER-INDIUM ALLOYS

6.1 Introduction

The hydrogenation of αβ-unsaturated aldehydes to form unsaturated alcohols has been thoroughly studied due to their importance in the production of fine chemicals, precursors in pharmaceutical industry and flavoring products (59). Thermodynamically, hydrogenation of unsaturated aldehydes is known to favor hydrogenation of the carbon-carbon double bond resulting in the production of the saturated aldehyde, generally the unwanted product, and therefore, kinetic control is desired (60). The degree of selectivity of unsaturated aldehydes to unsaturated alcohols is proportional to the size of the substituents present on the aldehyde’s carbon chain (69). Due to the fact that acrolein is the smallest chain unsaturated aldehyde, hydrogenation of acrolein presents a challenge since it lacks the bulky constituents that make hydrogenation of higher aldehydes easier (69) (62). Hydrogenation of acrolein to allyl alcohol (propenol) has been done on an industrial scale using Meerwin Pondorff Verley reactions (where the hydrogen source is isopropanol) with high selectivity (196). However, these processes are not environmentally friendly and require a number of steps that produce a considerable amount of waste (69). Hence, there would be a strong economic and environmental benefit to production of allyl alcohol from acrolein by a direct single step mechanism using a heterogeneous catalyst.
Selective hydrogenation of acrolein has been examined over a variety of late $d$-band transition metals (68) (61) (197) (64). However, Ag has been found to the best catalyst as more traditional hydrogenation catalysts (i.e. Pd) tend to activate C-C bond dissociation in the case of acrolein (62) (This is not a problem for hydrogenation of higher $\alpha$-$\beta$ unsaturated aldehydes).

Another important variable studied has been particle size. In the case of selective hydrogenation of acrolein over gold catalysts, it has been shown that both the selectivity and activity increase with increasing particle size (65). On silver catalysts, the increase of size has also been shown to increase activity and selectivity towards allyl alcohol (66; 198). The presence of large (111) terraces is speculated to provide sites that leads to packing of acrolein in a configuration conducive to hydrogenation of the C=O functionality (68). However, in contrast to those studies, Bron et al. found that small nanoparticles (2.5 nm diameter) yielded higher allyl alcohol selectivity than larger nanoparticles (14.2 nm diameter) and extended surfaces (60). The authors suggest that the higher activity and selectivity of the nanoparticles is related to the presence of defects which adsorb oxygen which leads to Ag$^+$ sites that adsorb acrolein.

Similarly, the hydrogenation of acrolein is highly sensitive to the total pressure. At pressures below 100 mbar no allyl alcohol is formed (60) (67). However, Claus et al. have found that increasing the total pressure from 10 to 20 bar has been shown to increase selectivity by 8% (to 42%) (199). However, further increases in pressure beyond 20 bar has no significant effect on the selectivity (199).
Previously, there have also been suggestions that sub-surface oxygen (or coadsorbed oxygen) could play a role in determining selectivity. Bron et al. have found that pretreatment in oxygen (air) results in an increase in the activity (60). In this work, oxygen was observed to have a positive effect on selectivity by increasing it from 29% to 42% (60). However, it is not totally clear from this work what the effect on selectivity is since the comparisons were made at highly different conversions. An explanation offered for the role of oxygen in the Ag catalyst was the potential of it perturbing the electronegativity of the surface and creating low coordination adsorption sites. Rosch et al. have used DFT calculations to determine that subsurface oxygen will change the interactions of the intermediates in acrolein hydrogenation with the surface so as to flip the selectivity from propanal to allyl alcohol (62). Rosch et al. considered adsorption of acrolein with coadsorbed hydrogen atoms on Ag(110) and showed that hydrogenation can occur through hydrogenation at four points: the terminal oxygen of acrolein or at any of the three carbon atoms. Hydrogenation of the terminal oxygen results in the formation of hydroxyallyl (H₂C=CH-CHOH) while hydrogenation of the carbon of the aldehyde functionality leads to the formation of allyloxy (H₂C=CHCH₂O). Further hydrogenation of hydroxyallyl or allyloxy leads to the formation of the desired product, the unsaturated alcohol, allyl alcohol. In contrast, hydrogenation of the double bond can lead to the formation of either 1-formylethyl (H₃CCHCOH) or 2-formylethyl (H₂CCH₂COH). Further hydrogenation of 1-formylethyl or 2-formylethyl leads to the formation of the saturated aldehyde, propanal. By modeling a Ag(110) surface with a sublayer of oxygen, Rosch demonstrated that the outcome of oxygen treatment affects both the activity and selectivity by lowering the barrier to hydrogen dissociation and shifting the stability of key intermediates on the surface (62).
Selectivity seems to be closely related to the strength of adsorption of the acrolein molecule to the surface, as well as that of the final products. The Ag(110) surface binds the acrolein molecule very weakly with an energy of only -13 kJ/mol (62). This is also the same trend of the final products which are also weakly adsorbed onto the Ag surface. Presence of oxygen also hinders the stability of the intermediate 2-Formylethyl on the surface (62). After hydrogen and acrolein have been adsorbed to the surface, the reaction paths towards allyl alcohol and propanal on Ag(110) are all exothermic, showing the importance of the structure of the surface in the selectivity. In contrast to the behavior of acrolein on silver and gold, strong adsorption in Pt(111) surfaces has the effect of hydrogenating the unsaturated aldehyde to saturated alcohol (63) implying that the selectivity can be manipulated if the adsorption strength can be changed. Murillo et al. have demonstrated by altering the catalyst with a monolayer of a 3d metal, different yields of propanal, propenol and propanol are achieved (200). By using single crystals, the interaction with the support is eliminated and the creation of a controlled pseudomorphic monolayer is possible. The experiments utilized either a 3d-Pt-Pt(111) or Pt-3d-Pt(111) configuration (3d metals: Co, Ni, Cu) which is used to obtain HREELS and TPD to decipher adsorption geometry and product yield. The preferred product, allyl alcohol, had poor selectivity on all alloys with structure 3d-Pt-Pt(111). Selectivity to allyl alcohol on Pt-3d-Pt(111) was maximized on Pt-Ni-Pt(111) upon hydrogen treatment. Hydrogen pre-treatment of the Pt-Ni-Pt(111) bimetallic presented a peak at 1569 cm\(^{-1}\) which was assigned to di-\(\sigma\)-C-O geometric configuration of acrolein, thus facilitating activation of the C=O bond. In contrast, Pt-Co-Pt(111) pre-treated with hydrogen has both, di-\(\sigma\)-C-O and di-\(\sigma\)-C-C vibrations, hence no increase in the yield to allyl alcohol was observed with the treatment. Adsorption in different orientations and
sites was examined using DFT. Similar adsorption energies were reported for all Pt-3d-Pt(111)
which were all weak in the ranges of -0.4 kJ/mol to -13.7 kJ/mol while structures of 3d-Pt-
Pt(111) had significantly greater adsorption energies in the ranges of -24.2 kJ/mol to -78.1
kJ/mol. Results of the DFT calculations suggests that the strong adsorption energies of the 3d-
Pt-Pt(111) are responsible for the less favorable yields of allyl alcohol when compared then to
their Pt-3d-Pt(111) counterparts. The underlayer of 3d metal is shown to lower adsorption
energies even when compared to pure Pt(111) (BE = -22.7 kJ/mol). These strong adsorption
energies are also believed to be responsible for the breaking of the acrolein carbons chain
(200). Although these experiments are carried at ultra-high vacuum conditions and low
temperatures (200 K – 300 K) compared to industrial conditions, they bring insightful
explanations as to the geometry of the adsorption of acrolein as well as the importance of the
composition of the surface where the reaction takes place.

Claus and Schlogl have found that alloying Ag with another metal may also contribute
favorably toward improving selectivity. Lucas and Claus studied the effect of alloying Ag with In
supported on SiO₂ (69). Samples prepared by impregnation with an aqueous solution using
different precursors and types of silica were tested for hydrogenation of acrolein. Among the
most selective samples, Ag supported on Porasil A silica gave a selectivity of 48% towards allyl
alcohol at a conversion of 79% at 473 K and 2 MPa. The pure silver catalyst had a particle size of
7.7 ±3.0 nm that was measured using TEM (69). The authors also produced a AgIn sample with
weight loadings of 9% Ag and 0.7% In supported on SiO₂. The sample of AgIn was reported to
have a particle size of 5 ± 1.5 nm and at 98% conversion of acrolein, the selectivity towards allyl
alcohol was measured to be 60%. Furthermore, under liquid phase reaction conditions (P= 5
MPa, T= 453 K), the AgIn catalyst was shown to have a selectivity of 75% towards allyl alcohol at a temperature considerably lower than the one used for the gas phase hydrogenation (T= 513 K gas phase) (69). Characterization of the AgIn catalyst with XPS shows the presence of In, In$_2$O$_3$, as well as metallic Ag and Ag$_2$O. The reduction temperature had an impact on the structure of the catalyst. At a reduction temperature of 603 K, a peak at 2θ = 39.8˚ appears which is consistent with the presence of a Ag$_3$In alloy (69). Although In clearly impacts the selectivity to allyl alcohol, its precise role in the reaction mechanism is not well understood. Alloying Au with In also improves the selectivity of acrolein hydrogenation reaction from 34% on Au/ZnO to 63% on Au-In/ZnO (61). TEM results indicate that Indium covers the terraces of Au and leaves only the edges and corners uncovered. The authors postulate that the active site for hydrogenation of the C=O bond is therefore at the corners and edges of the nanoparticle (61).

Theoretical results offer a different explanation of the role of indium in the Ag catalyst. He et al. studied the reaction of acrolein (cis-isomer) hydrogenation using Au(110) and In/Au(110) to approximate stepped surfaces in which a surface atom of Au was replaced with an indium atom (64). For Au nanoparticles supported on ZnO, the indium was reported to adsorb preferably on terraces rather than edges (61) thus influencing the choice of He et al. to replace a surface atom of the open surface (110) of Au with In. Calculations as to the adsorption on top of the surface or incorporation of the In atom into the Au surface concluded that inclusion of In into Au is favored by 35 kJ over adsorption on top of surface (64). On supported Au catalyst, the reaction was conceived to take place on the low energy terrace facets of the particle for C=C activation and on edges for C=O activation, thus inclusion of In potentially increases selectivity by blocking active sites on the terrace sites of the nanoparticle (61). Similar
to the Ag catalyst, acrolein has a weak interaction with Au (40 kJ/mol) and desorption of products occurs easily at reaction conditions (12 kJ/mol for propanal and 41 kJ/mol for allyl alcohol) (64). Indium was found to interact with the terminal oxygen of the C=O functionality more strongly than Au by 53 kJ/mol which also draws the acrolein molecule closer to the surface (64). On the pure Au(110) surface the two dominant paths towards wanted and unwanted products are through the hydroxyallyl and 2-Formylethyl intermediates, respectively, but a change in preferred path occurs when In is included on the catalyst. For the In substituted Au(110) surface, the dominant pathway towards allyl alcohol shifts such that formation of allyloxy is favored and the second hydrogenation step becomes rate limiting. Calculations presented by He et al. show that the presence of indium reduces the activation barrier of the C=O bond but does not affect C=C bond hydrogenation. Therefore the authors conclude that indium inclusion in the Au surface does not turn off the reactivity but rather attracts the acrolein molecules towards the terrace sites for reaction and that the undercoordinated edge does not aid in selective hydrogenation (64).

Another DFT study of Au (211) surface shows that the acrolein’s C=C bond has a weak interaction with atoms located at steps (Eads = 21 kJ/mol) (197). In contrast, the C=O functionality does not interact with the step atoms at all (197) suggesting that the edge sites lead to lower selectivity to allyl alcohol formation. On Pt(211) the step site is also preferred, as the acrolein molecule adsorbs via the C=C double bond (Eads = 157 kJ/mol) about 60 kJ/mol more strongly than on a terrace site. On Pt(211) the desorption of allyl alcohol was found to be important to the overall rate due to the strong adsorption energy of the final products onto the surface (76 kJ/mol for propanal and 140 kJ/mol for allyl alcohol) (197). In addition, on Pt(211)
the barrier for hydrogenation of hydroxyallyl was shown to favor the formation of the enol over allyl alcohol by approximately 19 kJ/mol (197), although the enol is not a stable species in the gas phase but it has been shown to be stabilized by bonding to metals (201).

We propose to study four models of silver based catalyst in order to understand alloying and size effects. Ag(111) will be used as a model for a large catalyst particle whereas a stepped surface, Ag(221), will be used to simulate the less coordinated atoms that are found in high percentage as the nanoparticle size decreases. Both Ag3In, and AgIn2, will be used to examine the effects of alloying and the role of In in improved selectivity. For the conditions at which the reaction is typically studied, Ag3In and AgIn2, are possible phases of silver-indium alloys (202).

6.2 Methodology

Density functional theory calculations were carried out using the Vienna Ab Initio Simulation Package (VASP) (37) (38) (39) (40). A plane-wave basis set with a cutoff energy of 400 eV and projected augmented wave pseudopotentials (47) (48) were used in all calculations. The Perdew-Burke-Ernzerhof (PBE-GGA) form of the correlation and exchange energy was used in all calculations (51) (52). All calculations are carried out with a 7 x 7 x 1 Monkhurst Pack kpoint grid, except the AgIn2 (110) surface which was carried out using a 6 x 5 x 1 kpoint grid (81). Starting with the optimized bulk structures, a six-layer surface was cleaved and optimized. For silver and Ag3In, the (111) plane was chosen as the most stable whereas for AgIn2 the (110) plane was chosen. To observe the effects of defects a Ag(221) surface was cleaved as well with six layers. All surfaces were relaxed in the upper four layers and the bottom two layers were
fixed to simulate bulk properties. Approximately 4 layers of vacuum separated the six-layer slabs in the z-direction. Geometries were judged to be optimized when the forces were within a convergence tolerance of 0.025 eV/Å. Transition state calculations were carried using the nudged elastic method to find the lowest energy transition point. Vibrational frequency calculations were used to confirm the presence of a single imaginary frequency associated with the transition state.

In order to look at electronic interactions between atoms, the CASTEP DFT code was used, in particular the modules for EELS and DOS within it. CASTEP possesses a module which allows for simulation of an EELS (XANES) spectra based on overlap integral of the core state and the final state (189) (54) (55) (53) (56). The core state is evaluated using an all electron calculation of an isolated atom, whereas the pseudowave function for the final state is generated by an ultrasoft pseudopotential calculation within CASTEP. Gaussian broadening of 0.2 eV was applied to mimic the instrument broadening and the effect of smearing due to the finite lifetimes of the final states and the fact that calculations necessarily involve a finite number of k-points.

6.3 Results

Adsorption of acrolein on the different orientations and positions has been examined on Ag(111) to determine a favorable location as well as on the other three surfaces. Energies of adsorption of the different sites for Ag(111) are reported in Table XI. For reference purposes, the carbons are labeled as C1, C2, and C3, being C1 the carbon bonded to the oxygen atom. In
all cases, the binding of acrolein to the surface is weak as has been determined previously by Lim et al. on Ag(110) (62). However, it has been suggested by Illas et al. that acrolein can favorably interact with itself at high coverage (0.25 ML) such that a “head to tail” orientation is adopted such that the C=O functionality interacts with the surface in a p(4×2) configuration (68). The results of Illas et al. suggest that previous experimental results of Bron et al. can be explained by the presence of a high coverage (and favorable orientation) at high pressure leading to high selectivity.

Table XI Adsorption energies of acrolein onto Ag(111)

<table>
<thead>
<tr>
<th>Adsorption Site</th>
<th>Energy of Adsorption (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1C2 bridge</td>
<td>-0.14</td>
</tr>
<tr>
<td>C1C2 FCC Hollow site</td>
<td>-0.13</td>
</tr>
<tr>
<td>C1C2 HCP Hollow site</td>
<td>-0.12</td>
</tr>
<tr>
<td>C1C2 Atop</td>
<td>-0.07</td>
</tr>
<tr>
<td>C1C2 HCP Hollow site (perpendicular to surface)</td>
<td>-0.06</td>
</tr>
<tr>
<td>O bridge</td>
<td>-0.07</td>
</tr>
</tbody>
</table>
Hydrogenation can be initiated at the oxygen or any of the three carbons (C1, C2, or C3). Following a simplified reaction path proposed by Rosch et al. (62), hydrogenation of acrolein was carried on all four surfaces to produce either one of four stable intermediates, hydroxyallyl, allyloxy, 2-formylethyl, or 1-formylethyl. The first two intermediates can be further hydrogenated to produce allyl alcohol and the last two are intermediates of the paths towards the unwanted product, propanal. A summary of the reaction paths used is shown in Figure 63.
Images of the surfaces studied are shown in Figure 64. As a starting point, gas phase of hydrogen, acrolein and the clean surface are used as reference. On all surfaces, hydrogen dissociation is considered the first step of the reaction due to the difficulty of this step on all surfaces.

The paths depicted on the left correspond to the desired products whereas the ones on the right are towards the unwanted product, propanal. Similar adsorption energy trends were observed on all other surfaces. Reaction paths for each surface are depicted in Figures 65 to 68.
Using Ag(111) as a base of comparison, the reaction pathway results are shown on Figure 65. The first barrier to overcome along any hydrogenation reaction pathway is the dissociation of hydrogen. The dissociation of hydrogen at a coverage of 0.5 ML on Ag(111) is found to be 1.32 eV which is similar to the one calculated on Ag(110) of 1.30 eV (203). In the previous studies of Rosch et al., He et al. and Yang et al., the dissociation of hydrogen is considered separately (62) (64) (197). However, it is clear from previous calculations of Rosch et al. and Barrio et al. that the largest barrier to overcome is the initial dissociation of hydrogen (203) (204). We find that in our examination of the pathway to form allyl alcohol that formation of hydroxyallyl and allyloxy have very similar activation barriers (only differing by 0.16 eV) implying that both intermediates may form. Thermodynamically the first hydrogenation towards allyl alcohol favors the formation of allyloxy by 0.44 eV. The second hydrogenation shows a greater difference between the two paths, as the barrier for hydrogenation of allyloxy is only 0.33 eV whereas hydrogenation of hydroxyallyl has a barrier of 0.81 eV. Allyl alcohol is weakly bound to the surface (0.29 eV) and therefore desorbs readily once formed. For the unwanted product, propanal, the difference between the paths involving 2-formylethyl and 1-formylethyl is clear from the initial hydrogenation step, in which the formation of 1-formylethyl has an activation energy lower than that for 2-formylethyl formation by 0.47 eV. Thermodynamically, the formation of 1-formylethyl is also preferred by 0.85 eV. The second hydrogenation step towards propanal shows that formation from either intermediate has a low barrier and is exothermic. Propanal is bound even less strongly (0.06 eV) to Ag(111) than allyl alcohol. Therefore, unlike the Pt catalysts, desorption of the final products has no influence on the selectivity since it is not a rate limiting step.
The potential energy surface of the selective hydrogenation of acrolein over Ag(221) is presented in Figure 66. Unlike the Au(221) stepped where a preference for acrolein adsorption exists at terrace or steps via the C=O and C=C groups respectively, there is no easily determined preference for adsorption of acrolein at a particular surface site on Ag(221). Therefore, the initial positions of the reactants were set near the step edge in an attempt to determine the effect of coordination on the reaction mechanism. As in the case of the Ag(111) surface,
hydrogen was found to have weak energy of adsorption onto different sites on the Ag(221) surface being only physisorbed onto it by 0.08 eV on the bridge site of the step. Hydrogen dissociation on Ag(221) is carried on the 3-fold hollow sites on top of the step of the surface to facilitate the hydrogenation of acrolein by placing the hydrogen in sites within a reasonable proximity to the position of acrolein. The activation barrier for the hydrogen dissociation decreases to 1.26 eV and the reaction enthalpy also decreases to 0.40 eV. Similar to Ag(111), the reaction pathways towards allyl alcohol on Ag(221) have nearly identical barriers whether the first hydrogenation forms allyloxy or hydroxyallyl. As on Ag(111), allyloxy is the thermodynamically favored intermediate only by 0.13 eV over hydroxyallyl on Ag(221). The second hydrogenation step requires a higher barrier for hydrogenation of allyloxy as opposed to hydroxyallyl such that the path through hydroxyallyl is actually lower in energy by 0.22 eV at the transition state. Once again, desorption of the allyl alcohol molecule should be facile as the unsaturated alcohol is bound by only 0.26 eV to the Ag(221) surface. On the paths towards propanal, there is a large difference between the initial hydrogenation barriers to form 2-formylethyl (1.65 eV) and 1-formylethyl (0.37 eV) suggesting that only formation of 1-formylethyl will be possible. 1-formylethyl formation is exothermic (-0.83 eV) and its formation should be favored over the hydroxyallyl and allyloxy as well. Although the barrier for the second hydrogenation step to form the final product, propanal, is higher than barriers for hydrogenation of allyloxy or hydroxyallyl, the transition state energy is actually lower than the transition state energies for those pathways when looking at the overall potential energy surface.
Figure 66 Reaction paths on Ag(221).

In order to understand the role of alloying, two surfaces with different ratios of Ag to In were examined. Previously Ag$_3$In was suggested as a possible phase formed in AgIn catalysts (69). Therefore the Ag$_3$In(111) surface was chosen as a model for the alloy catalyst since the (111) surface is the lowest energy fcc surface and its structure provides a direct comparison with Ag(111). At a first glance, the dissociation of hydrogen has a slightly higher barrier on Ag$_3$In (111) than on Ag(111) by 0.1 eV. Acrolein adsorbs in a similar fashion to Ag$_3$In(111) as it does on a pure Ag surface (i.e. no preferential adsorption was observed to surface In through the C=O
bond). The pathway to allyl alcohol through the hydroxyallyl intermediate has lower barriers for both hydrogenation steps by 0.29 eV and 0.19 eV for first and second hydrogenations respectively, when compared to the allyloxy pathway on the same surface. However, thermodynamically, the first hydrogenation is more favorable on the allyloxy path by 0.62 eV whereas the final hydrogenation is favored for hydroxyallyl. For the final product, allyl alcohol, the adsorption energy is 0.29 eV. For the paths to propanal, the first hydrogenation to 1-formylethyl has a much lower activation barrier (E_{act} = 0.58 eV) than the barrier to form 2-formylethyl (E_{act} = 1.05 eV). Similarly, for the second hydrogenation, the difference between the transition state energies on the potential energy surface is 0.42 eV in favor of the formation of propanal through 1-formylethyl. Thermodynamically, the first hydrogenation to 2-formylethyl is thermoneutral (\Delta E = -0.01 eV). Meanwhile, the first hydrogenation step of 1-formylethyl is favored thermodynamically by 0.52 eV. The second hydrogenation which forms propanal from either, 2-formylethyl or 1-formylethyl, is thermodynamically favored for both intermediates. The final product, propanal, is weakly bonded to the surface, requiring virtually no input of energy to desorb from Ag$_3$In(111) (0.04 eV).
To assess the effect of alloying, a more dramatic effect might be seen by increasing the indium content of the alloy. Therefore, we chose AgIn$_2$ (tetragonal, D$I_4$/mcm) as a candidate structure for further examination of the role of indium in promoting selective hydrogenation. The (110) surface of AgIn$_2$ was determined to be the lowest energy surface among the low Miller index surfaces of AgIn$_2$ and was used a representative surface. The AgIn$_2$(110) surface also presented the lowest activation barrier for the hydrogen dissociation (1.17 eV). Paths towards allyl alcohol have similar activation barriers, 1.30 eV and 1.40 eV for the formation of
hydroxyallyl and allyloxy respectively. The second hydrogenation step to form allyl alcohol has very low barriers ($E_{\text{act}} < 0.42 \text{ eV}$) starting from either intermediate. The reaction energy of both paths is close to thermoneutral, with hydroxyallyl first hydrogenation only being favored by 0.09 eV over allyloxy path. The second hydrogenation is a downhill process of over 1.25 eV from either intermediate. Comparison of first hydrogenation steps shows formation of 1-formylethyl to have the lowest activation barrier among all four paths (0.99 eV). Thermodynamically, the path through 1-formylethyl is a downhill process with first and second hydrogenation energy of reaction of -0.57 eV and -1.27 eV respectively. On the other hand, the energy barrier for the first hydrogenation of 2-formylethyl is 0.36 eV higher than that of 1-formylethyl, and thermodynamically less favorable by 0.46 eV compared to that of 1-formylethyl, suggesting that initiation of hydrogenation towards propanal occurs primarily by the 1-formylethyl path. However, the transition state energy of the second hydrogenation of 1-formylethyl is actually very similar to that for 2-formylethyl or hydroxyallyl (and just 0.06 eV lower than allyloxy hydrogenation). Both propanal ($E_{\text{ads}} = -0.06 \text{ eV}$) and allyl alcohol ($E_{\text{ads}} = -0.35 \text{ eV}$) are very weakly adsorbed on the AgIn$_2$(110) surface.
6.4 Discussion

Silver has never been regarded as a traditional hydrogenation catalyst (60). In fact, dissociation of hydrogen is among the highest barrier steps of the acrolein hydrogenation reaction and the process is endothermic as well. The high dissociation barrier and unfavorable reaction enthalpy implies a high partial pressure of hydrogen is required in order to achieve a suitable coverage of hydrogen on the surface for reaction (60). Comparison of the hydrogen dissociation step of the reaction on all four surfaces is shown in Figure 69. It is clear that on all
surfaces studied herein the dissociation of hydrogen is a thermodynamically unfavorable step with a reasonably high barrier. The presence of steps in the surface improved the activation barrier of the hydrogen dissociation by only 0.06 eV and lowers the reaction enthalpy to 0.42 eV over Ag(221). The reduction in the barrier and the reaction enthalpy over the Ag(221) is expected as undercoordinated surface atoms can frequently act as reactive sites for dissociation reactions (205). It is clear that the geometric effect that influences the hydrogen splitting on pure silver catalysts is minimal. One should expect that smaller Ag nanoparticles may be more slightly active for acrolein hydrogenation than large Ag particles, but this is not what we observe. Although the potential energy surface suggests that hydrogen dissociation is kinetically important (and in fact rate determining), experimental data indicate that some other aspect of the mechanism involving acrolein must be critical to catalyst performance since the reaction order for acrolein is usually found to be close to 1 (66) (67).

In addition, it is observed that the activation energy of hydrogen dissociation on Ag(111), Ag$_3$In(111), and AgIn$_2$(111) surfaces do not follow a clear trend as the quantity of indium increases. The difference in activation energy between Ag(111) and AgIn$_2$(110) is negligible (0.06 eV), and it only increases to 0.1 eV when shifting to the Ag$_3$In surface, therefore there is very little effect on the activation energy of hydrogen dissociation upon inclusion of indium at any ratio. A similar reduction in the hydrogen dissociation barrier is seen over Ag(221) as the activation energy is lowered only by 0.06 eV, meaning that a change in the geometry also has a negligible effect on the activation barrier of the hydrogen dissociation.
The reaction enthalpy for hydrogen dissociation on the Ag(111) surface is 0.49 eV, but increases to 0.62 eV on Ag$_3$In(111). In contrast, a shift in the opposite direction is observed on AgIn$_2$(110) where the hydrogen dissociation energy is lowered to 0.40 eV. Changes in the enthalpy due to presence of In are only of 0.13 eV and 0.09 eV for Ag$_3$In(111) and AgIn$_2$(110) respectively, which are minimal changes. Inclusion of indium at a higher fraction in the catalyst also results in facilitating the dissociation slightly, but does not explain the increase in
selectivity that is observed when In is present. Therefore, we must examine the hydrogenation steps involving acrolein and other surface intermediates in more detail to understand how alloying and structure influence activity and selectivity.

6.4.1 Hydroxyallyl reaction path

When comparing the Ag(111) surface and the Ag(221) surface, the stepped surface has a significant effect on the reaction enthalpy as the reaction to form hydroxyallyl is somewhat more exothermic with a $\Delta E = -0.25$ eV. However, there is also an increase in the activation barrier to 1.01 eV over the Ag(221) surface (as opposed to 0.81 eV). The second hydrogenation step producing allyl alcohol is exothermic on both surfaces but there is a decrease in the activation energy on Ag(221) when compared to Ag(111) by 0.17 eV. Clearly for this path, the stepped surface of Ag does not have a significant advantage in stabilizing the transition states to form the hydroxyallyl intermediate to impact either selectivity or activity.

When examining the potential energy surface of the selective hydrogenation reaction over Ag$_3$In(111), we observe only a small effect from alloying. The barrier for hydrogenation is similar on Ag(111) ($E_{\text{act}} = 0.80$ eV) and Ag$_3$In(111) ($E_{\text{act}} = 0.74$ eV) while the reaction enthalpy is a bit higher on the alloy surface ($\Delta E = 0.07$ eV vs. $\Delta E = 0.06$ eV). However, further increasing the content of indium to AgIn$_2$ leads to a thermodynamically favorable formation of hydroxyallyl ($\Delta E = -0.07$ eV) but the barrier to hydroxyallyl has climbed significantly to 1.30 eV. The greater difference between the indium alloyed surfaces and the pure silver comes in the second hydrogenation of hydroxyallyl to allyl alcohol, in which Ag(111) has a barrier of 0.81 eV that is
lowered to 0.48 eV and 0.42 eV for Ag$_3$In(111) and AgIn$_2$(110) respectively suggesting that even though the first hydrogenation does not see a benefit on the higher In to Ag alloy, the second hydrogenation is definitely aided by the Ag-In alloy.

6.4.2 Allyloxy reaction path

For the stepped Ag(221) surface, the activation energy is very similar to that of Ag(111), (E$_{\text{act}}$ = 1.01 eV vs. E$_{\text{act}}$ = 0.96) but the reaction enthalpy becomes more exothermic by 0.24 eV. The small increment in the activation energy and the increase in the exothermicity of the enthalpy change on the Ag(221) surface, suggests that this first hydrogenation is not very sensitive to the surface structure and is an early transition state which is relatively unperturbed by the changes in reaction enthalpy. For the second hydrogenation step on Ag(221), the activation energy is greatly increased to 0.86 eV, but the transition state energy is well below the energy of the transition state for the first hydrogenation step suggesting that the second hydrogenation should not exhibit a high degree of rate control (or selectivity control) (206).

The effect of alloying on allyloxy formation can be seen in examination of the first hydrogenation barrier. The barrier increases with the increase in the amount of indium with a barrier of 0.96 on Ag(111), increasing to 1.03 eV on Ag$_3$In(111) and finally a barrier of 1.40 eV on AgIn$_2$(110). However, the reaction enthalpy does not follow the same trend as the formation of allyloxy on Ag$_3$In(111) is more favorable than on Ag(111) by 0.41 eV, an unexpected result given the increase in barrier. When comparing the AgIn$_2$(110) surface to Ag(111), the reaction enthalpy difference for allyloxy formation is negligible (ΔE = 0.16 eV). For the second
hydrogenation step in which the aldehyde functionality is further hydrogenated to produce allyl alcohol, all are downhill processes thermodynamically, as in the case of hydroxyallyl path. For both Ag(111) and Ag₃In(111), the transition state for hydrogenation of allyloxy is lower in energy than that for hydroxyallyl. On AgIn₂(110) the situation is reversed, but the energy difference is very small (0.07 eV) and the transition state energies are well below those of the first hydrogenation. This result suggests that the second hydrogenation plays little role in the observed selectivity. On all surfaces, the activation barriers for the first hydrogenation of acrolein to allyl alcohol tend to be higher for allyloxy than hydroxyallyl even though the allyloxy intermediate is favored thermodynamically. This suggests that a great majority of the propenol produced might have been conceived by the hydroxyallyl path rather than the allyloxy pathway.

6.4.3 2-Formylethyl reaction path

Surprisingly, even though this path leads to the undesired product which is thermodynamically favored, the first hydrogenation step is not thermodynamically favored with a ΔE=0.12 eV on Ag(111). The first hydrogenation step to produce 2-formylethyl appears to have a strong structure sensitivity as the reaction enthalpy is now exothermic (ΔE = -0.27 eV) on Ag(221). However, while more exothermic, the activation barrier actually increases on the stepped surface by 0.59 eV. The barrier for second hydrogenation step to form propanal from 2-formylethyl is lower than the first hydrogenation step on both surfaces.

An examination of the potential energy surfaces of acrolein hydrogenation on the alloy surfaces also indicates that this pathway to propanal is unlikely. On Ag₃In(111), the first
hydrogenation step is actually thermoneutral with only a negligible change in the activation barrier of -0.01 eV. On AgIn$_2$(110), the reaction enthalpy decreases by 0.23 eV but the activation energy increases by 0.29 eV. Activation barrier increases upon alloying by 0.67 eV and decreases by further increase of In to 0.44 eV. Both alloy surfaces show an increase in the activation energy for the second hydrogenation step, although the barrier over Ag$_3$In(111) is actually higher than that over AgIn$_2$.

6.4.4 1-Formylethyl reaction path

In all the cases studied, the hydrogenation of acrolein to propanal takes place through the 1-formylethyl intermediate. On Ag(111) the formation of 1-formylethyl is exothermic with $\Delta E = -0.73$ eV while formation of 2-formylethyl is endothermic. On Ag(221) this reaction is even more favorable than on Ag(111) by 0.10 eV and is similarly favored over 2-formylethyl formation. In addition, the activation barriers for hydrogenation to 1-formylethyl are consistently lower than the barriers to formation of 2-formylethyl. For example, on Ag(111) the activation barrier for the formation of 1-formylethyl is only 0.59 eV as opposed to 1.07 eV for 2-formylethyl formation. The activation energy is even lower on the Ag(221) surface ($E_{\text{act}} = 0.37$ eV). Formation of the unwanted product, propanal, from the intermediate 1-formylethyl is less exothermic on the Ag(221) surface ($\Delta E = -0.95$ eV) which is 0.18 eV higher than the energy on Ag(111). In addition the activation energy is also not benefited by the presence of the step since it doubles when moving from Ag(111) to Ag(221) (0.46 eV to 0.92 eV). It is clear that the change in the geometry of the catalyst has an impact on the activation barriers as well as adsorption strength of the intermediates. Overall the reaction through the 1-formylethyl path
sees opposing effects on the first and second hydrogenation steps in which the first hydrogenation is easier on Ag(221) but the second hydrogenation is more difficult as the barrier increases and the reaction is less exothermic as we move from the (111) surface to (221) surface of Ag.

Introducing a second metal, In, the enthalpy sees a reduction with the presence of indium from -0.73 eV on Ag(111) to -0.52 eV and -0.57 eV for Ag$_3$In(111) and AgIn$_2$(110) respectively for the hydrogenation of acrolein to 1-formylethyl. A different effect is seen in the activation energy, where on Ag(111) this hydrogenation has an activation energy of 0.59 eV and remains the same on Ag$_3$In(111) and then increased by 0.40 eV on AgIn$_2$(110). Both the activation energy and the reaction enthalpy suggest that the presence of indium would hinder the first hydrogenation step in this path.

The second hydrogenation of 1-formylethyl to propanal is highly favored thermodynamically on all three surfaces, with Ag$_3$In(111) the most exothermic of the alloys (ΔE = -1.44 eV). A similar trend to that of allyloxy is seen in which the intermediate point (Ag$_3$In(111)) does not have an intermediate effect, rather a novel effect in which the ΔE is not in between the values of Ag(111) and AgIn$_2$(110). For AgIn$_2$(110), the enthalpy of the reaction is increased from -1.13 eV (Ag(111)) to -1.27 eV, but Ag$_3$In(111) rather than having a change in reaction enthalpy between those values, it has an even more exothermic reaction with ΔE = -1.44 eV. Activation barriers on the other hand have an increasing trend with the increase of indium from 0.46 eV (Ag(111)) to 0.62 eV (Ag$_3$In(111)) and 0.91 eV AgIn$_2$(110)), thus increase of the content of In makes it harder for the reaction to reach the final product, propanal, from the
1-formylethyl intermediate point. Summarizing this path, both hydrogenation steps are hindered on the alloys for the 1-formylethyl path and the presence of indium, therefore, lowers the rate of propanal formation.

6.5 Effect of structure

Comparing the reaction paths of hydroxyallyl and allyloxy towards the desired product of propanal on the Ag(111) and Ag(221) surfaces, the first hydrogenation step changes by increasing the activation barrier for acrolein to hydroxyallyl by 0.21 eV from Ag(111) to Ag(221) whereas the allyloxy path only sees an increase of 0.05 eV on the step surface. Although the change in the reaction energy and the activation barrier is greater for hydroxyallyl with the change in the surface from Ag(111) to Ag(221), both paths are equally viable with allyloxy being slightly more thermodynamically favored than hydroxyallyl by 0.13 eV.

The second hydrogenation barrier has a greater increase on the allyloxy path to allyl alcohol (0.53 eV) and a decrease in hydroxyallyl one (-0.17 eV) when comparing the Ag(111) to the Ag(221). Overall for the paths towards allyl alcohol, on Ag(111) the energetically preferred path is allyloxy while on Ag(221) there is no clear distinction between the two paths (hydroxyallyl and allyloxy) meaning that both pathways are plausible. The preferred path on Ag(111) (allyloxy) only sees a benefit with the change in geometry from (111) to (221) on the thermodynamics of the first hydrogenation, but this is dampened with the increased difficulty of achieving the final product on the second hydrogenation.
For the hydrogenation of acrolein towards propanal, the presence of the stepped surface does not change the pathway as 1-formylethyl is always the preferred intermediate. For this reaction path, the first hydrogenation barrier is lowered on the Ag(221) surface (by 0.22 eV) and thermodynamically favored by 0.10 eV over Ag(111) while the second hydrogenation to achieve propanal is actually hindered by this surface with an increase in activation energy of 0.46 eV and a decrease in ΔE of 0.18 eV.

Changing the surface to Ag(221) will facilitate the formation of 1-formylethyl over hydroxyallyl or allyloxy, mainly due to the lower activation barrier as well as the higher stability of this intermediate on the surface. Upon reaching the intermediate point, the step surface actually makes it more difficult to form propanal from 1-formylethyl with an increase in activation barrier and a decrease in reaction energy. Although second hydrogenation of allyloxy has an increase in activation barrier on the Ag(221) surface, the energy required for this hydrogenation is slightly lower (by 0.06 eV) than that needed for the 1-formylethyl path and in the case of hydroxyallyl is even lower (by 0.28 eV), thus if the intermediates are formed, production of allyl alcohol would be favored by the availability of two reaction paths and the lower barrier of hydroxyallyl than 1-formylethyl.

6.6 Effect of alloying

Overall, there is a noticeable benefit to the reaction paths involving hydroxyallyl and allyloxy with the inclusion of indium. As stated before, on Ag(111) the most likely path towards allyl alcohol is that of allyloxy mainly due to the smaller (by 0.48 eV) activation barrier on the
second step than hydroxyallyl. By alloying Ag with In in a 3:1 ratio, the hydroxyallyl path now also becomes a possible path mainly due to the instability of the hydroxyallyl on the surface which reduced the required energy to complete the path to allyl alcohol. The described changes imply that the Ag$_3$In(111) alloy surface not only is beneficial to the already preferred path but it also opens the possibility of producing the desired product through an alternate pathway. Due to the large barriers for the first hydrogenation towards allyl alcohol on AgIn$_2$(110), the activity of an alloy with a high indium content is expected to be low. The inclusion of indium at both ratios 3:1 and 1:2 benefits the 2-formylethyl path thermodynamically, but does not change the preferred pathway away from 1-formylethyl path on any of the three surfaces considered. If the reaction follows the 1-formylethyl path, for the first hydrogenation inclusion of indium at the 3:1 ratio does not alter the activation barrier but it decreases the exothermic character of the step by 0.21 eV. On AgIn$_2$(110) the reaction enthalpy is relatively the same as in Ag$_3$In(111) (-0.57 eV and -0.52 eV respectively) but the activation energy is increased by 0.40 eV. The second hydrogenation also sees an increasing activation barrier as the amount of indium increases.

Overall the inclusion of some indium has been shown to aid the hydroxyallyl pathway towards allyl alcohol while altering the energetics of the 1-formylethyl path and thus changing the selectivity from propanal toward allyl alcohol (although the preferred product remains propanal). Inclusion of indium at the 1:2 ratio not only makes it more difficult to follow the paths towards propanal but it also hinders the first hydrogenation of the allyloxy and hydroxyallyl intermediates and reduces the activity.
Electronic structure effects

From the results of the potential energy surface, one can see that the presence of indium should increase the selectivity of the catalyst but reduce its activity. To understand why the alloy helps improve selectivity, we have analyzed the PDOS of Ag(111), Ag₃In(111) and AgIn₂(111) as shown in Figure 70. The d-band center is shown to shift away from the Fermi level as the indium content increases from -3.92 eV on Ag(111) to -4.20 eV on Ag₃In(111) and finally to -4.46 eV on AgIn₂(111). From Hammer and Norksov’s d-band theory, if the host’s d-band center will shift away from the Fermi level the surface is less reactive (3). On the other hand, an underbonded atom will experience a shift towards the Fermi level and thus become more
reactive. Previous studies done by our group have shown that the density of states near the Fermi level is related to the shifts and intensity of the X-ray Adsorption Near Edge Structure. Density of states and XANES can help determine the type of interaction between silver and indium at an electronic level. Figure 70 also shows the XANES calculated for the pristine surface structures of Ag(111), Ag₃In(111), and AgIn₂(110). It is clear that as the indium quantity increases there is a shift towards lower energy and a change in the shape of the leading edge. A similar shift is seen in the experimental sample supported on SiO₂ when including In at an approximate ratio of Ag to In of 3:1 as seen in Figure 71. The changes are attributed to the density of states near the Fermi edge. However from Figure 65 is obvious that there are very few available states near the Fermi level, and that as the indium quantity increases, the center of the d-band is shifting away from the Fermi edge. Since it does not appear that the density of the d-states near the edge is responsible for the changes in the XANES, other phenomena must be governing the observed spectra. Figure 72 depicts the s-PDOS of the three AgₓInᵧ structures. Figure 72 reveals that there is an increase in the s-density of states near the Fermi level (particularly at about 2 eV above the edge) for the alloys where In is present and that this effect is more pronounced as the content of In increases. Based upon this result, we speculate that the observed changes in the absorption edge may be due to increases in the availability of empty s-states which are allowed transitions from core p-states according to the selection rules. In addition, we have performed a simple Bader charge analysis to examine how charge may be redistributed in this system. Unlike d-band transition alloys in which little charge transfer between elements is observed, Bader analysis shows there is significant charge
transfer from Indium to silver (-0.33 for Ag₃In(111) and -0.82 for AgIn₂(110)) showing an electronic interaction between silver and indium.

Figure 71 Experimental XANES of Ag and AgInₓ supported on SiO₂.
6.8 Conclusions

The hydrogenation of acrolein was investigated on four surfaces: Ag(111), Ag$_3$In(111), AgIn$_2$(110), and Ag(221). Adsorption of acrolein has been proven weak on all surfaces, with adsorption energies best characterized as physisorption. Hydrogen dissociation barriers were high on all surfaces and its adsorption is endothermic compared to gas phase hydrogen.
Comparison of the reaction pathways most likely followed by acrolein for both the desired and unwanted products, suggests Ag$_3$In(111) as the most favorable catalytic surface for allyl alcohol formation among those studied here. There are only minor geometric effects that are expressed as changes in the exothermic state and activation energy of the different hydrogenation steps. The effect of alloying strongly influences the energetics of the pathways to propanal formation while resulting in smaller increases in the barriers to the formation of the intermediates along the path to allyl alcohol.
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