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SCHREYER HONORS COLLEGE

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GAMMA BRASS STRUCTURES AS CATALYST FOR SELECTIVE HYDROGENATION
OF CROTONALDEHYDE

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ABSTRACT

The selective hydrogenation of crotonaldehyde to form either crotyl alcohol or n-butylaldehyde was studied using Density Function Theory (DFT). Previous work had demonstrated the promise of a palladium-zinc bimetallic catalyst, in both a monomer and trimer form, in favorably hydrogenating the carbon-oxygen double bond. The study was completed through analyzing the calculated energies of the molecular systems and using their relative values to determine favorable arrangements. The results indicate a strong preference for the adsorption of the carbon-carbon double bond over the carbon-oxygen double bond on both the palladium-zinc monomer and trimer surfaces. Further analysis demonstrated that neither surface catalyst would promote the complete reaction of crotonaldehyde to n-butylaldehyde. Both systems resulted in unsurpassable activation barriers leading the catalyst to be inactive for the hydrogenation of crotonaldehyde.

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Chapter 1

Introduction

Reduction of chemical species is arguably one of the most important chemical reactions currently being studied. A reduction reaction involves the transfer of an electron from one atom to the next which subsequently involves a decrease in the oxidation state of the reduced atom. In order for a reduction reaction to take place, a chemical species must be capable of donating an electron to a different atom of interest. The donating species is known as a reducing agent due to its role of reducing the oxidation state of the new atom. The donation of the electron leads to an association between the two atoms being formed which results in a new bond.¹

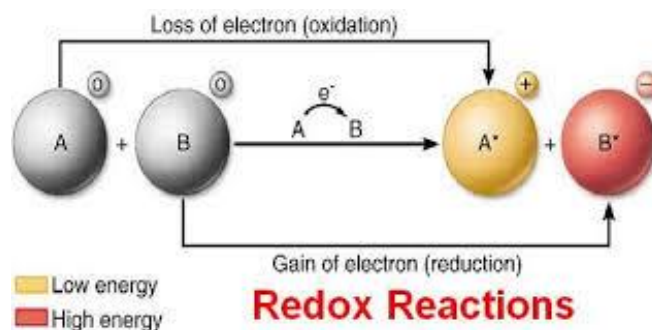


Figure 1 Visualization of a Redox Reaction.

One of the most useful reducing agents in this class of reaction is hydrogen because of its simple nature and its clean potential. Hydrogen is a diatomic element of the chemical formula H_2 . During its dissociation, hydrogen breaks into two individual hydrogen atoms without any other impurities or side products. This makes hydrogenation one of the most vital catalytic methods in synthetic chemistry. The reaction is extremely versatile because it applies to a variety

of functional groups with high conversions. When a molecule reacts with hydrogen it is classified as a hydrogenation reaction which is what the focus of this paper will be on.

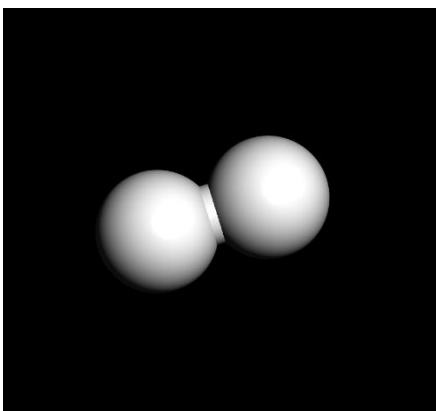


Figure 2 MSI Visual of Diatomic Hydrogen

One of the most applicable area for hydrogenation reactions occurs within the oil and refinery fields of study. Oil is comprised of a variety of hydrocarbons that can be unsaturated which leave the molecule susceptible to be hydrogenated into its saturated form. Hydrogenating is a relatively easy task, but in many hydrocarbons there are multiple unsaturated sites which are desired to be selectively hydrogenated.² The purpose of selecting a specific site is because each reaction will result in the production of a different chemical species. These species can have vastly different chemical properties which leads to certain products being more valuable than others.

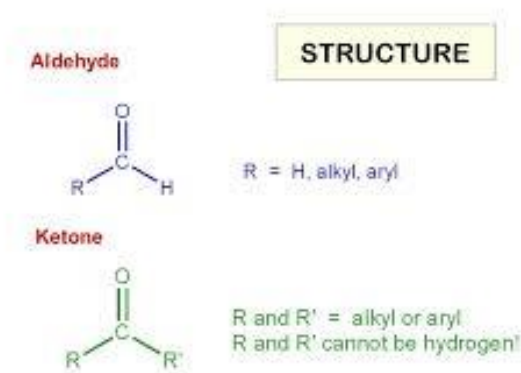


Figure 3 Comparison of Aldehydes and Ketones

In the oil industry, the two main classes of hydrocarbons that tend to be involved in hydrogenation reactions are ketones and aldehydes. The importance of these two types of chemical compounds is the presence of at least one carbon-oxygen double bond (C=O). Molecules connected with a double bond are good oxidation agents which makes them very likely to participate in hydrogenation. In these molecules, the carbon atom that is bonded to the oxygen has two remaining bonds that can consist of hydrogen or alkyl or aryl substituents. To be a ketone neither of these groups can be a hydrogen while aldehydes are classified with either one or both groups being hydrogen. The other type of bond that can be present in the R- group in these molecules that make them very interesting in the topic of selective hydrogenation is the presence of carbon-carbon double bonds (C=C). Once hydrogen is introduced to the system, the hydrogen ions must choose between hydrogenating either the C=C or the C=O double bonds which is where selective hydrogenation occurs. Typically, it is the hydrogenation of the C=O double bond that is favorable in producing a product of greater value along with being the harder species to hydrogenate. In more complex systems, the study of hydrogenation between competing C=C double bonds along with competing C=O double bonds can be observed but lend

themselves to being more difficult to promote a significant degree of selectivity. Also, another difficulty comes in the form of being able to promote one selectivity over the other to such an extent where the competition ceases to exist causing a relatively pure product being formed over a mixture of the two species. The ability to generate a relatively pure product can lead to a drastic increase in profits, eliminating the requirement for additional purification steps. One such use is adding hydrogen to petroleum products and aromatic reduction in order to stabilize the compound. Hydrogen is used to saturate unstable olefins and di-olefins which otherwise would produce undesirable gums in storage that are very costly to remove.³ Hydrogen is also utilized in refining a variety of petroleum compounds.

Being that some of the most profitable chemical compounds are in the field of oil, the phase of the reactant of interest is typically in the liquid state. Hydrogen on the other hand will be found to be in the gaseous state unless a significant amount of energy is used to lower the temperature and increase the pressure to lead to either a compressed liquid or liquid phase of hydrogen. Reaching this state is not a commercially feasible for the hydrogenation of liquid hydrocarbons and therefore the reaction between these compounds also find themselves in the class of two-phase reactions.

In heterogeneously-catalyzed chemical reactions, the reactants are transformed into the products through a sequence of step by step elementary reactions. The overall reaction can be theorized using a reaction mechanism which describes the plausible pathway the reactants take to form the final products. The reaction pathway for this class of reactions involves the adsorption of reactants onto the catalyst's surface, surface reactions among the absorbed species and intermediates, and finally the desorption of the product. For hydrogenation reactions using a surface catalyst, the overall reaction involves two reactants, a type of unsaturated hydrocarbon

and a hydrogen molecule, reacting to form a single product, a saturated hydrocarbon. From here, there are a handful of elementary reactions that must take place in between these forms. The first is the dissociation of the diatomic hydrogen into two hydrogen atoms which must be absorbed onto the catalyst surface. Then, one of the hydrogen atoms must attack a carbon or oxygen molecule that is involved in a double bond in the hydrocarbon of interest (if hydrogenating a C=C double bond then either of the carbons may be attacked and if hydrogenating a C=O double bond then either the carbon or oxygen of this bond may be attacked). During this attack, a transition state is created where the hydrogen begins binding to the atom of interest, but the double bond still exists. Once the hydrogen is fully bonded to the atom then the double bond is weakened; thus, becoming a single bond giving a new intermediate structure. The second hydrogen then attacks the other atom in the original double bond which again transitions into another transition state before becoming the final, hydrogenated product.⁴ This product is then desorbed from the catalyst surface creating the stand-alone product.

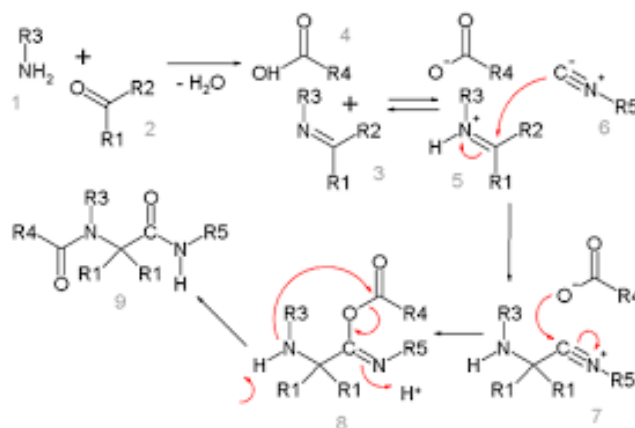


Figure 4 Example Reaction Mechanism Pathway

The major use of a reaction mechanism is being able to visualize the steps a reaction must follow in order to achieve the final product. Each step can be studied in order to determine the feasibility of the steps and the spontaneity of the reaction. This is accomplished through the

energy of structures being analyzed to determine the barriers the reaction pathway must overcome. As seen below, the potential pathway of a multi-step chemical reaction is explained using an energy diagram which plots the potential energy stored within the molecule along the reaction pathway:

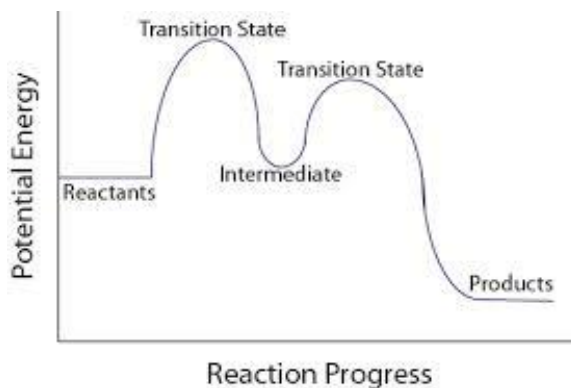


Figure 5 General Reaction Coordinate Energy Diagram

The energy difference between the reactant and transition state and the energy difference between an intermediate and transition state are classified as activation energies. These energy differences are the major barriers the reaction needs to overcome. The transition state will always be at a potential energy higher than the original reactant energy and the transition state will also be at a potential energy higher than the intermediate during the intermediate steps. The magnitude of the energy difference is one of the major contributing factors to the kinetics of the reaction. If the energy difference is small, then the reaction will proceed at a faster rate (faster kinetics) than if the energy difference is large. Too high of an energy difference can also prevent the reaction from even occurring due to an energy barrier that is too extreme to overcome. In terms of competing reactions, large differences in the activation energy can result in only one reaction occurring. Although one of the reactions may be able to overcome the energy barrier,

the relative difference may be substantial enough to conclude that the less favorable reaction can be assumed negligible.

Studying these reactions started with simple observations and quantitative measurements in order to determine the rates of any reaction along with the energy required through analysis of heat differences in the system. Running these reactions becomes both a timely and expensive exercise due to the equipment necessary along with the chemicals needed. Often, a hypothetical reaction is proposed to be determined infeasible after further study and reaction attempts. Quantum mechanics has become very popular in the field of chemical reactions due to the various applications of its calculations. These calculations revolve around determining the probabilistic nature of an arrangement utilizing wave functions.⁵ For chemical reactions, this approach has the ability to predict the total energy of a system of electrons and nuclei by analyzing all the potential interactions between the subatomic particles. By looking at the most probable locations, the overall energy of a specific arrangement can be determined and utilized to predict the ability of a reaction to occur.

The computational technique that is widely utilized in these quantum mechanical calculations is known as density functional theory (DFT).⁶ This theory utilizes the Schrödinger equation with its associated Hamiltonians and eigenvalues to solve for a wave function that describes the electronic structure of the system of interest. The determined wave function is then used to model the behavior of the atoms in the reaction and calculate the associated energies. The energies can then be compared in order to determine the feasibility of the reaction. If there is reason to believe the reaction is favorable, then further chemical reactions can be run using the reactants.

Activation energies, or activation barriers, are unique because they are flexible. Another chemical compound can often be used to help lower the energy of the intermediate structure; thus, lowering the energy difference from the original structure. Often, catalysts can be used to help promote chemical reactions that wouldn't occur at normal conditions. In industry, catalyst can be used to help increase the kinetics of a reaction to help promote productivity. As for selective hydrogenation reactions, catalysts can not only be used to lower the activation energy of the hydrogenation reaction but also to help drive the hydrogenation of a certain double bond in the hydrocarbon. This provides the opportunity to use a catalyst to increase the selectivity of the hydrogenation of certain C=C double bonds over other C=C double bonds. The more applicable case is the use of a catalyst to promote either the hydrogenation of a C=C double bond over a C=O double bond or vice versa. Typically, it is the C=O double bond that is viewed as more valuable, but these catalysts help with producing a product of greater purity. The use of hydrogenation to form an unsaturated alcohol is useful in the production of a variety of species in the cosmetic, pharmaceutical, and specialty chemical product fields.⁷ The current catalyst commonly used for this reaction is a metal hydride but due to environmental, economic, and technical difficulties a different method is preferred.

The class of catalysts that are best suited for this application are surface catalysts.⁷ These catalysts lower the energy of the activation barrier by allowing the reactants to bind to the surface of the catalytic structure. The energy is reduced due to the catalyst making it easier for the reactants to make contact with each other and/or altering the structure so the energy of the intermediate is lower than before. The addition of a catalyst adds additional steps to the reaction mechanism of a hydrogenation reaction. First, the hydrocarbon that is desired to be hydrogenated will need to bind and stay on the surface. There is an adsorption energy associated with the

binding of the molecule on the surface of the catalyst. There is also a desorption energy which is the change in energy of the system if the molecule was to unbind from the catalyst's surface. The adsorption and desorption energies have the same values, opposite in sign. Therefore, if energy is released upon the binding of the molecule then it would take the same amount of energy to be adsorbed for the unbinding of the molecule. Another step that must be included as well is the diffusing of the bound hydrogen atoms to the hydrocarbon of interest. The movement of the hydrogen has its own energy associated with it and when it moves it follows a path that involves an intermediate structure (and therefore a subsequent energy barrier it must overcome).

A surface of interest in selective hydrogenation reactions is a bimetallic surface. When a monometallic catalyst has been used, the formation of an unsaturated aldehyde has been the outcome.⁸ The addition of a second metal has been shown to give the catalyst properties that result in higher selectivity and stability through its use in the hydrogenation reaction allowing the possibility for selectivity to an unsaturated alcohol. These surfaces consist of a certain metal element that is infused with another creating an intermetallic. The main element in the catalyst analyzed for this reaction is zinc and can be combined with metallics including copper, silver, and nickel along with many other elements.⁹ A unique aspect of these surfaces is the presence of a γ -brass phase for the system. Rather than a random arrangement of the two (or more) metallic elements throughout the surface, the surface is well-defined and periodic.

Of the metallic elements that can be combined with zinc to make an intermetallic, palladium has shown a lot of promise in terms of demonstrating properties that promote selective hydrogenation.¹⁰ Catalytic functions of Pd-Zn were studied in the conversion of methanol at Hokkaido University.¹¹ Specifically, with methanol, it was a C=O double bond that was being hydrogenated which leads to great interest in this type of catalyst.

The γ -brass catalyst has seen use in removing acetylene from ethylene through the selective hydrogenation of acetylene over the hydrogenation of ethylene to ethane.¹⁰ A Ni-Zn catalyst was the one of interest in these experiments. One key aspect that has been noted of the γ -brass structures is the formation of specific crystals dependent on the composition of the metal alloy. NiZn, Zi_4Zn and Ni_5Zn_{21} catalysts were analyzed to determine the effects on ethylene selectivity to find that the arrangement of the atoms plays a role in the subsequent reaction.¹¹ In terms of the Pd-Zn catalyst, two forms of the arrangement were found where the palladium atoms appear as isolated monomers in the surface or can take the form of a connected trimer.¹⁰ The formation of these organized structures in the surface of the catalyst were determined to be caused by the composition of the bimetallic structures. Pd_8Zn_{44} would result in the monomer form of the surface (Pd8) and Pd_9Zn_{43} would result in the trimer form of the surface (Pd9).

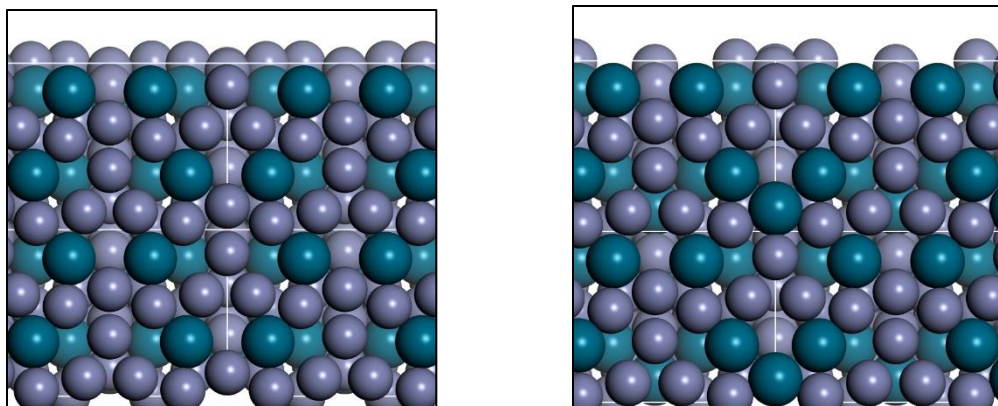


Figure 6 Pd8 Surface (left) vs. Pd9 Surface (right)

Crotonaldehyde is a common chemical used for the application of catalyst for selective hydrogenation due to its simplistic nature and the presence of both a C=C and C=O double bond in proximity.¹² The compound itself is used as a precursor in the production of fine chemicals such as certain food preservatives, manufacturing of resins, suitable solvent, and production of thiophene, quinaldines, pyridines, pharmaceuticals, dyes, and pesticides.

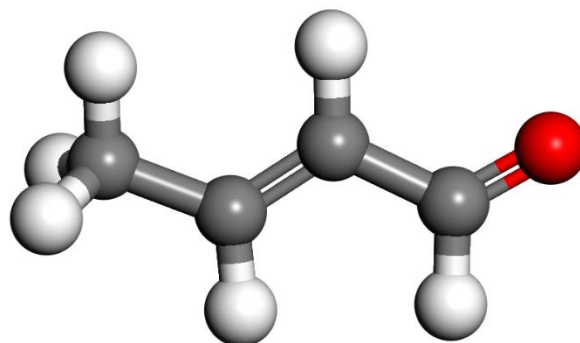


Figure 7 MSI Visualization of Crotonaldehyde

Due to the widespread uses of crotonaldehyde and the ability to use this compound for comparative analysis between C=C and C=O hydrogenation, a lot of studies have been run testing the effects of many catalysts on the hydrogenation reaction. One such study involved the use of TiO₂ to favorably hydrogenate the C=O double bond.¹³ The problem with this work was the necessity of another element to induce activation of the catalyst. Research has been accomplished showing the ability of platinum, nickel, and gold particles to play a crucial role in the catalytic reaction but also requires high temperature to achieve the reduction resulting in a costly reaction.¹⁴ Other bimetallic catalysts that consists of platinum variants have also been tested for the hydrogenation of the C=O double bond of crotonaldehyde but resulted in the production of only butyraldehyde.¹⁵ The mechanism has been proposed that selective site blocking along with reduction in the platinum ensemble size could lead to the deactivation of sites responsible for hydrogenating the C=C double bond but results showed that a more suitable catalyst must be used.¹⁶ ZnO has been one such catalyst but only has been shown to have a low

conversion which again prevents a practical process. Throughout literature many attempts have been made at selectively hydrogenating the C=O double bond but finding a catalyst suitable for a practical production of the unsaturated alcohol remains an issue.^{17,18,19}

The purpose of this paper is to analyze the possible use of palladium-zinc catalysts for the hydrogenation of crotonaldehyde with a focus on achieving a high selectivity in favor of the hydrogenation of the C=O double bond through determination of the activation energies along the reaction pathway.

Chapter 2

Methods

All calculations were completed using the Vienna ab initio simulation program (VASP) which evaluated the electronic structure through the expansion on a plane wave basis. The energy and charger distribution of the atomic system were obtained as results from this evaluation. These values were then also utilized in later calculations. The VASP was used to find the transition state between two atomic structures by first optimizing the arrangement of the structures. The coordinate layout supplied by VASP was then translated into an image file of the state which was created and analyzed through Materials Studio 7.0.

A plane wave basis set was with an energy cutoff of 400 eV. VASP supplied a projected augmented wave (PAW) pseudopotentials that were also used. A Monkhorst-Pack grid was used with a $6 \times 6 \times 1$ k-point setting. Calculations were performed on both a $\text{Pd}_8\text{Zn}_{44}$ and a $\text{Pd}_9\text{Zn}_{43}$ surface. There were three layers of the surface in each surface cell.

The limitations of this computational model revolve around the inability to account for the length and time of real systems. Real systems consist of constantly moving molecules, but this model cannot account for these dynamics and instead assumes a stationary system. The physical basis for this assumption is that the atoms in the intermetallic are extremely concentrated in order to represent an atom being in each surface cell, but this assumption is unrealistic.

The electrochemical reaction that these calculations focused on was the complete hydrogenation of crotonaldehyde to crotyl alcohol and to n-butyraldehyde over each palladium catalyst. Prior to the reaction, the optimized structures of both the crotonaldehyde and the

surfaces were obtained. Then, the adsorption reaction was optimized similarly. The first step in the hydrogenation reaction is the conversion of crotonaldehyde to an intermediate species. The reaction step was modeled and the activation barrier was calculated.

The method utilized for calculating the activation barrier of an electrochemical reaction steps starts with optimizing the initial and the final states of the reaction step. The initial state consisted of the crotonaldehyde molecule adsorbed to the palladium atom on the catalytic surface and a hydrogen atom (H^*) that has been adsorbed and diffused next to the crotonaldehyde. The final state consisted of the crotonaldehyde bound to the hydrogen creating an intermediate state.

Once these states were optimized, a CI-NED (climbing image -nudged elastic band) transition states search was executed. The resulting structure was only considered to be the true transition state if certain criteria were met. The first was that this state is the maximum energy structure found on the energy curve; therefore, the tangential forces needed to be equal to about a value of zero. Secondly, frequency calculations were performed, and the presence of a negative frequency proved that the transition state had been calculated.

The energy values of all the structures were then analyzed to determine the plausibility of the overall reactions.

Chapter 3

Results and Discussion

The methods in this project were developed using the hydrogenation of crotonaldehyde over a palladium-zinc catalyst surface. Specifically, the selective hydrogenation of crotonaldehyde to either crotyl alcohol or n-butanal were of interest using either a monomer formation of palladium-zinc catalyst (which will be referred to as Pd8) or a trimer formation (which will be referred to as Pd9). The entire process of the hydrogenation and use of the catalyst were analyzed and the associated energies were calculated to use for comparisons and determine if one surface would prove useful in the selective hydrogenation of crotonaldehyde. The reactions of interest are visualized below:

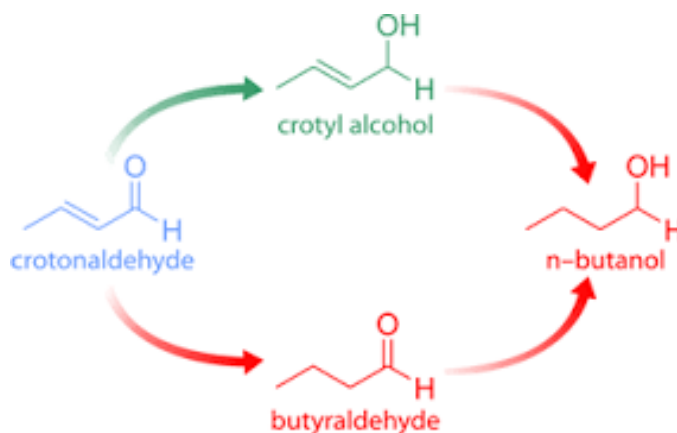


Figure 8 Crotonaldehyde Hydrogenation Reactions

Initially, the basic molecule of crotonaldehyde needed to be optimized to determine the structures' calculated energies. Knowing the initial energies of the atomic systems allows for energy comparisons to be completed for future arrangements to determine the theoretical change of energy of the reaction. The energies of the initial structures of interest can all be visualized in Table 1.

Table 1 Optimized Energies of Different Structures

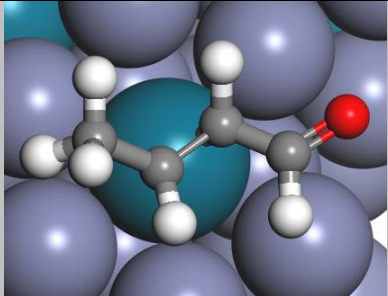
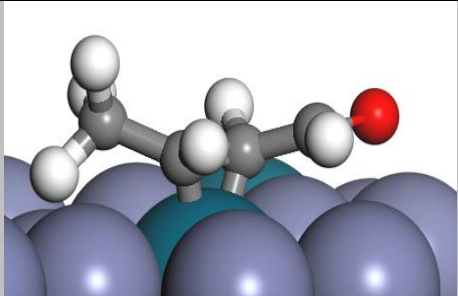
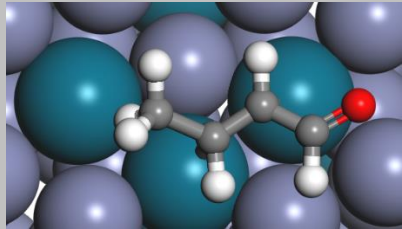
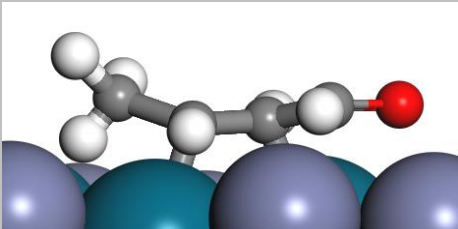
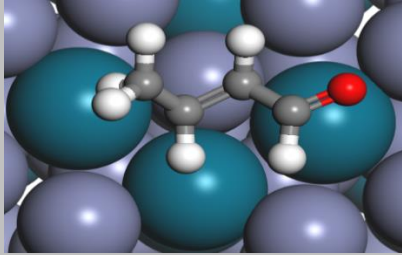
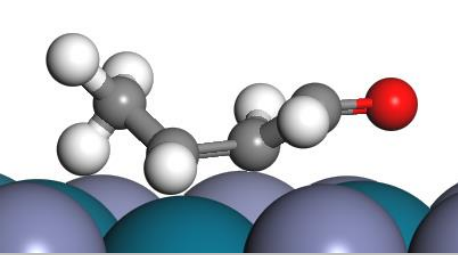
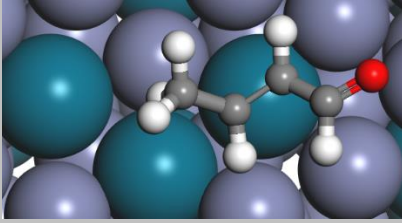
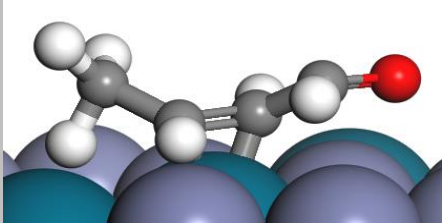
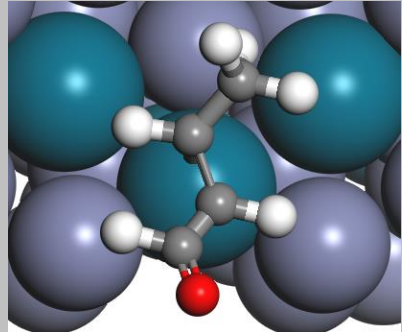
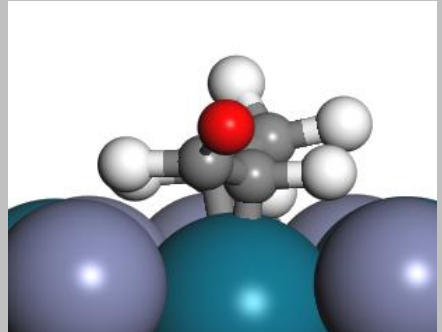
<i>Structure</i>	<i>Energy (eV)</i>
Crotonaldehyde	-64.11
Hydrogen	-6.77
Pd8 Surface	-135.69
Pd9 Surface	-144.45

Analysis of Adsorption Mechanisms

The first step in determining the possibility and feasibility of the hydrogenation reaction was to analyze the interaction of the crotonaldehyde molecule with the catalysts of interest. For the catalyst to have an impact on the reaction steps, the crotonaldehyde must be adsorbed onto the catalyst surface. The adsorption of crotonaldehyde is an endothermic reaction; therefore, energy is released upon completion of the reaction, so it is a spontaneous process. The goal was to have the palladium variant surfaces favorably only bind to one double bond of crotonaldehyde.

One aspect to note is there can be multiple ways the molecule can adsorb onto the surface. In the case of the Pd8 monomer, the molecule can only bind “atop” over the palladium molecule. In the case of the Pd9 trimer, the molecule was able to bind in a variety of ways which all needed to be tested to determine which system would yield the largest (negative) adsorption energy. The naming convention and visualization of the adsorption layouts can be seen below:

Table 2 MSI Visualizations of Adsorption Sites on Catalyst

<i>Adsorption Site</i>	<i>Top View</i>	<i>Front View</i>
Monomer		
Bridge		
Hollow		
Side-atop		
Top-atop		

Finding the largest adsorption energy arrangement was necessary because subsequently, the desorption energy is equivalent to the adsorption energy. This means it takes the same amount of energy to unbind the molecule on the surface as the amount of energy that was released upon adsorption. The larger the value the less likely the desorption reaction will be competitive enough to prevent further reactions on the catalyst surface. The calculated energy of all the arrangements can be seen in the below table:

Table 3 Adsorption Energies on Optimized Sites

<i>Absorption Site</i>	<i>Energy (eV)</i>
C=C monomer	-0.2240
C=O monomer	0.0789
C=C bridge	0.0595
C=C hollow	0.0712
C=C side atop	-0.1938
C=C top atop	-
C=O bridge	0.0617
C=O hollow	-0.0748
C=O side atop	-
C=O top atop	0.0281

The major find of these results is that the C=O double bond of crotonaldehyde does not bind to either the Pd8 or Pd9 surface under any arrangement. This is explained by there being no significantly negative energy associated with the absorption of the C=O double bond on either

surface during any arrangement. This shows the catalysts are unlikely to be practical for the conversion of crotonaldehyde to crotyl alcohol but shows there is an extremely high selectivity for the binding of C=C double bond. The adsorption energy on Pd8 monomer can be seen to be -0.224 eV while the “side-atop” adsorption on the Pd9 trimer was the most favorable configuration at -0.194 eV.

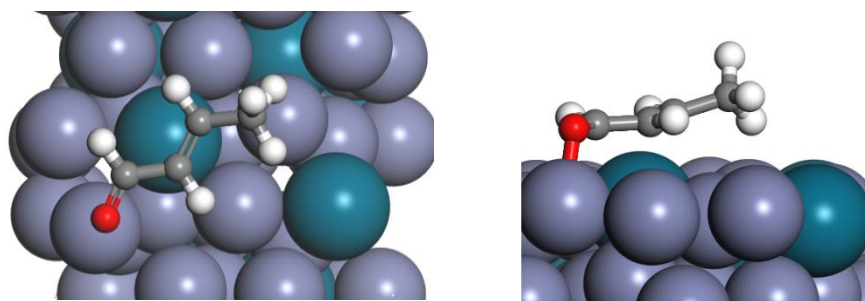


Figure 9 MSI Visualization of Oxygen-Zinc Interaction

An interesting trend appeared during the research which demonstrated that the oxygen on crotonaldehyde showed some interaction with the zinc molecules on the catalyst surface. The adsorption energy of this arrangement was calculated but no significant change in energy was observed.

Analysis of n-Butyraldehyde Reaction

Following successful determination of the best mechanisms for the C=C double bond adsorptions on both the Pd8 monomer site and the Pd9 trimer site, the hydrogenation reaction to n-butyraldehyde was analyzed. It was assumed that the initial adsorption energy of the hydrogen atom can be ignored; therefore, the proposed reactions began with the hydrogen already absorbed onto the surface of the catalyst on an adjacent palladium molecule. The analysis of the hydrogenation reaction followed the mechanism of an initial diffusion of the hydrogen and then

the first hydrogenation reaction. Following, a second hydrogen ion diffused into place and then the final hydrogenation occurred to complete the overall reaction. The activation barriers were found and compared to the adsorption energies to determine if the proposed reaction would be likely.

On the Pd8 monomer site, it was calculated that the initial diffusion activation energy had a value of 0.514 eV in comparison to the desorption energy of crotonaldehyde of 0.224 eV. Because of the drastic energy difference, it was assumed that the hydrogenation reaction would result in no reaction because the desorption reaction would easily outcompete it.

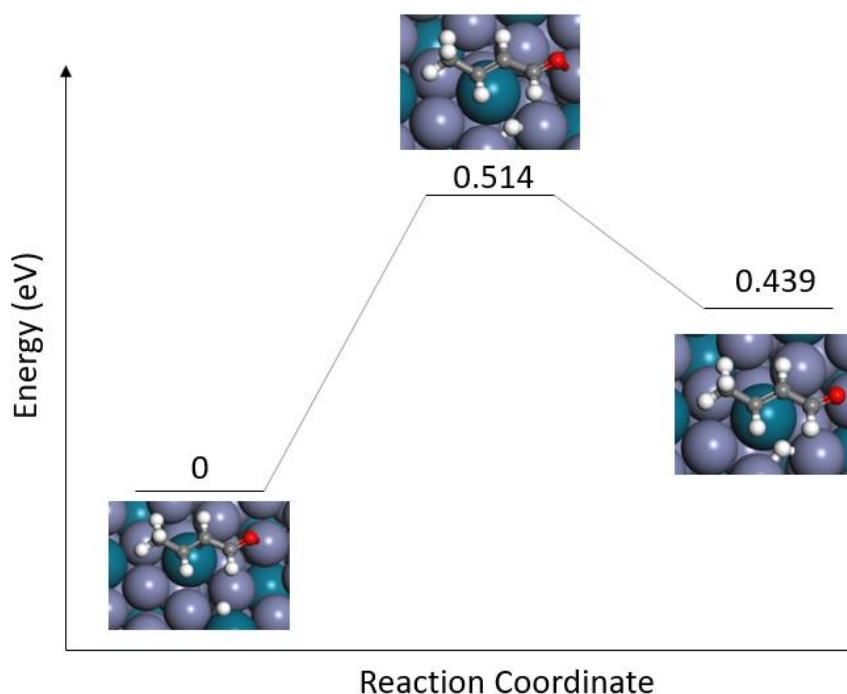


Figure 10 Pd8 Initial Diffusion Energy Diagram

On the Pd9 trimer site, it was calculated that the initial diffusion activation energy had a value of 0.245 eV in comparison to the desorption energy of crotonaldehyde of 0.194 eV. These values were similar enough that it was assumed the diffusion reaction would occur. The first

hydrogenation reaction had a calculated activation energy of 0.427 eV which in comparison to the desorption energy seems insignificant so the Pd9 catalyst is assumed to be inactive for the hydrogenation reaction.

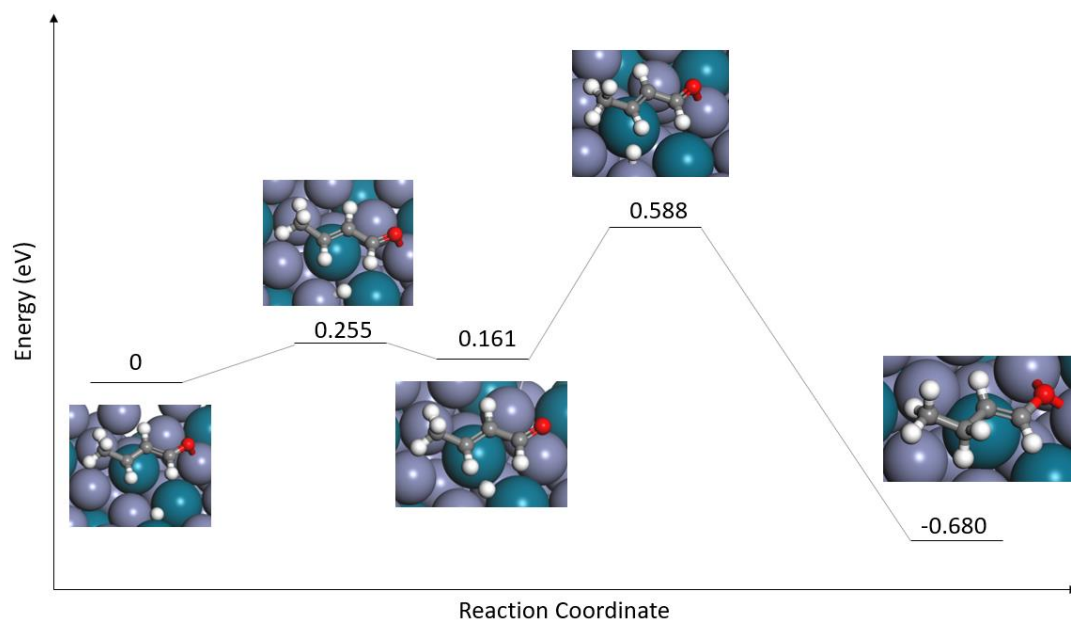


Figure 11 Pd9 Initial Hydrogenation Energy Diagram

Chapter 4

Conclusions and Future Work

The methods and calculations presented in this thesis were used to evaluate the ability of Pd8 monomer sites and Pd9 trimer sites to catalyze the selective hydrogenation of crotonaldehyde. The catalysts themselves were shown to be very successful at interacting with the C=C double bond of crotonaldehyde leading to adsorption onto the γ -brass surfaces. Also, the side-atop configuration of the adsorption on the Pd9 catalyst was found to be the most energetically favorable. As for the hydrogenation reaction overall, neither catalyst showed promise in being able to catalyze the reaction due to significant energy barriers remaining in the activation energy despite the presence of a catalyst. This was likely due to the presence of the large methyl group on one of the carbons along with other functional groups on crotonaldehyde which create a steric hindrance on the hydrogenation by preventing easy maneuvering of the hydrogen atom. Also, during the analysis only certain paths were analyzed for the diffusion of the hydrogen atom; therefore, the paths studied may have not been energetically favorable leading to these results.

Future work that can be pursued in this area would likely revolve around the result that these catalysts are highly selective for the C=C adsorption of crotonaldehyde; therefore, other reactions outside of hydrogenation could potentially be examined for the selective conversion of crotonaldehyde to valuable products on these catalysts. Other configurations of the crotonaldehyde on the surface can also be studied in order to help minimize potential steric hindrance of the hydrogenation reaction. Lastly, hydrogenation reactions of smaller molecules

than crotonaldehyde can be studied on these surfaces now that the selectivity of the catalyst has been confirmed computationally.

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