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PALLADIUM ZINC BASED INTERMETALLIC CATALYSTS TO PROBE HYDROGENATION ACTIVE SITE ENSEMBLES

A Thesis in

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by

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ABSTRACT

The intermetallic compound PdZn has shown promise for a vast range of applications in areas ranging from energy, environment, construction materials, methanol steam reforming, and corrosion resistance. Structure is one among the main factors that affects its performance. The intermetallic PdZn compound can allow for catalytically active Pd configurations to be isolated by an inactive Zn. These well-defined and isolated catalytic sites are explored in this study for catalysis of small molecule chemistries. The two main topics investigated in this study were the use of: (1) the Pd-Zn γ -brass phase to determine active site requirements for hydrogenation catalysis and (2) off-stoichiometry β_1 Pd-Zn phases to explore possible new active sites ensembles.

Our research group has previously used isotopically labeled ethylene in examining the acetylene hydrogenation selectivity from a feed containing both acetylene and ethylene. If propylene hydrogenation were to show similar catalytic rates to ethylene hydrogenation, we could replace labeled ethylene with propylene and save experimental time and resources. Evaluations for the potential of utilizing propylene in place of isotopically labeled ethylene for acetylene semi-hydrogenation in the presence of ethylene experiments on Pd-Zn γ -brass were performed using density functional theory (DFT) calculations. Ethylene and propylene were shown to adsorb similarly to the γ -brass surface when van der Waals forces were considered. Two possible hydrogen diffusion pathways were identified resulting in two possible hydrogen diffusion barriers over a Pd₃ trimer with co-adsorbed ethylene or propylene. With the possibility of each adsorbate having one of two paths, this suggests that the adsorbate identity will not alter the rates of hydrogen surface diffusion. The first hydrogenation step of the adsorbate showed similar activation energies for ethylene and propylene_C1 (hydrogenating the carbon with the additional methyl group) while

the activation energy of the hydrogenation of propylene_C2 was seen to be larger than that of ethylene and propylene_C1, suggesting it is less likely to occur. These results suggest that propylene has the possibility of being used as a surrogate for ethylene in hydrogenation reactions, though with subtle differences in hydrogenation rates.

Ternary Pd-M-Zn γ-brass catalysts could offer further selectivity control in hydrogenation through introduction of the additional M atom in Pd-M-Pd trimer active sites. Pd-M-Zn γ-brass materials were synthesized through solid state diffusion. The identity of the catalyst was characterized and confirmed through X-ray diffraction (XRD), Rietveld refinement, and ICP-OES equipment. The XRD confirmed that the synthesized catalyst contained the γ-brass phase. Rietveld refinement of the diffractogram confirmed atom locations/site occupancies of each element in the unit cell and that the ternary metal will appear as the central atom of the trimer site. Using the ICP-OES equipment to obtain the composition of each catalyst confirmed that the synthesized catalysts were near that of the intended compositions: Pd₉Zn₄₃, Pd₉CuZn₄₃, Pd₉AuZn₄₃, Pd₉AgZn₄₃.

The Pd-Zn β_1 phase has a relatively wide stability range over which some amount of Pd or Zn substitution can be made to perturb the stoichiometry away from the 1 to 1 PdZn base composition. We explored the surface sites that might be exposed in adding additional Pd atoms using DFT calculations. The upper Pd limits of the β_1 phase (Pd₉Zn₇ and Pd₁₀Zn₆) were examined to better understand possible bulk and surface constructions and their relation to each other in terms of stability. Five possible active site ensembles, which are (1) an "X" shape of five Pd atoms, (2) a Pd₃ triple, (3) off-set Pd monomers, (4) in-line Pd monomers, and (5) a Pd "box", were identified from low index facets. These active site ensembles resulted in surfaces that were both stoichiometric (number of atoms are multiple of that of the bulk composition) and nonstoichiometric surfaces, which affect the method of surface energy calculation. All stoichiometric surfaces resulted in active site ensembles with Pd atoms arranged in an "X" ensemble. On the other hand, the non-stoichiometric surfaces had the possibility of being any of the five possible facets. No surface could definitively be selected to be most energetically favorable to exist due to two non-stoichiometric surfaces with different active site ensembles (X and triple) that showed overlapping surface energies. Further testing of the stability of the active site ensembles performed through surface exchanges showed that all facets preferred to exist as the initially found "X" active site. Subsurface exchanges, on the other hand, revealed that many surfaces would preferentially have the Pd that was added to the Pd_1Zn_1 unit cell to appear on the surface. Therefore, it was deemed that excess Pd added to the PdZn beta phase would segregate significantly to the surface, leaving no unique active sites exposed.

This study will assist further research involving simulation of industrial feedstocks bound for ethylene polymerization, which utilized acetylene and expensive isotopically labeled ethylene. Synthesis and characterization of the ternary Pd-M-Zn γ -brass provided information on phase identity and site occupancies, which can be used for kinetic studies of ethylene hydrogenation to further understand the active site requirements. The findings that there are no unique active sites in Pd rich Pd-Zn β_1 phase surfaces indicated that this catalyst is not applicable for probing hydrogenation active site ensembles.

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CHAPTER 1 Intermetallic compounds and their uses in catalysis

1.1. Introduction: Historical perspective

Various facets in the growth of civilization has substantially been affected by the ubiquitous role of metals, such that the principal periods in human civilization are referred to based on the materials and metals that were pervasive during those times, such as the Stone age, Copper age, Bronze age, and Iron age. Civilizations in antiquity employed mainly eight metals: copper, gold, silver, iron, tin, zinc, lead, and mercury¹. Through investigations and numerous accidental discoveries, the characteristics of these native metals became evident and their usage has continuously been explored. Copper was the first metal that was widely used on a large scale, which was partly attributed to its abundance in nature. This was followed by major advancement in the various manipulations of the purity of copper and when it was discovered that mixtures of two metals, or alloys, were stronger than either of the individual metals leading to the invention of bronze¹⁻³. Among those, the alloy of tin and copper and alloy of lead and copper have marked the onset of the Bronze age. The technical discoveries (e.g., alloying of iron and carbon, hammering iron bloom, steeling, quenching, furnace design for melting, and casting) resulted in the transformation in property of iron that had heralded the Iron age; iron had been recorded to be the most useful and most widely used $metal^2$.

With the apparent benefits of mixing metals for improved chemical, mechanical and electrical properties came the discovery of the more modern metals such as beryllium, cadmium, chromium, molybdenum, tungsten, vanadium, magnesium, titanium, precious metals (iridium, rhodium, palladium, and platinum), and aluminum³. Some of the more common multimetallic compounds are brass, bronze, steel, copper-tin, and nickel-tin.

Multimetallic compounds can be further categorized as alloys or intermetallic compounds. As shown in Figure 1.1, alloy compounds are comprised of two or more metallic elements, which do not contain periodic, ordered crystal structures⁴. The atoms within the compound are random and may not be consistent between two samples of the same alloy. Intermetallic compounds are materials comprising of two or more metallic elements, in which the atoms are in a well-defined, ordered crystal structure^{5,6}. Compared to random alloys, stable and periodic isolated active sites are easily synthesized and reproduced^{6,7}.



Figure 1.1. Multimetallic compounds characterized to be intermetallic compounds or standard alloys (*Photo Source: European Space Agency, n.d.*⁴)

1.2. Intermetallic catalysts

Increased attention had been given to intermetallic compounds because of the promising potential as catalysts, thermoelectrics, and electrical conductors, among others and for the vast applications in the area of surface chemistry, construction materials, and corrosion resistance, among others. This study focuses on the potential of intermetallic compounds as catalysts as affected by structure effects rather than electronic. In catalysis, these intermetallic compounds allow for isolated catalytic sites, in which we can study the effect of structure in small molecule chemistries^{5,8-11}.

A catalyst is defined as a material or substance that transforms reactants into products through a series of uninterrupted and repeated cycle of elementary steps, wherein the catalyst participates while being regenerated to its original form at the end of each cycle during its lifetime¹². The key attributes of a good catalyst were enumerated¹³ to include: (1) good selectivity for production of the desired products and minimal production of undesirable byproducts, (b) adequate rates of reaction at the desired reaction conditions of the process, (c) stable performance at reaction conditions for long periods of time or can regenerate good catalyst performance by appropriate treatment of the deactivated catalyst after short periods, and (d) good accessibility of reactants and products to the active sites such that high rates can be achieved per reactor volume.

Intermetallic compounds are compounds that contain two or more elements possessing partly or completely ordered crystal structures that are different from those of constituent elements; the intermetallic compounds serve as precursors for skeletal catalysts or can be formed under reaction conditions and will thus, influence the catalytic properties significantly¹⁴. Intermetallic compounds have the high potential to narrow the materials gap in heterogenous catalysis because of its availability in various forms (nanoparticles, crushed powders and large single crystals)¹⁵. Ambruster et al. ¹⁵ contended that with the huge structural and electronic variety of intermetallic compounds come its huge potential in heterogenous catalysis for numerous catalytic phenomena.

Several related review papers^{6,8,14} also prove the notable increase and fast development in intermetallic compounds in heterogenous catalysis. A review article⁸ is directly related to the current study, which provides a review of intermetallic nano-crystal synthesis methods, characterization of catalytic multi-metallic surface, applications of intermetallic catalysts compared to pure metals and discussed the current challenges.

This current thesis draws heavily from an earlier research by Dasgupta¹⁶ at Rioux Lab in the Department of Chemical Engineering, Pennsylvania State University and is, in fact, an offshoot of this prior research. The extensive review⁸ on the growing application of intermetallic compounds in heterogenous catalysis and a portion of the research dissertation of Dasgupta¹⁶ served as the starting ground for the current study. The highlights of findings on the various research on Pd-Ag, Pd-Ga, Pd in Pd-Ga, Pd-Cu, Au-Pd, Pd-Al₂O₃, Pd-Ag/TiO₂, Pd-Si/SiO₂ to include activity and selectivity and the possible drawbacks for these intermetallics, among others, have already been compiled⁸ and will not be repeated here. Instead, the preceding provides a brief review on some of the research that may relate to the current study on the examination of possible higher Pd content active sites and utilization of the Pd-Zn based γ -brass phase as a model catalyst. This chapter does not intend to provide a comparative and extensive review but to present and to provide a general picture of some of the different research directions and ideas that relate to the current study. Other references are directly incorporated in the discussions in the preceding chapter.

Intermetallic formation with an active material with another inert component to form an ordered crystal structure have been shown to produce a unique and homogenous ensemble of active sites that can serve as adaptive sites for catalytic processes¹⁶⁻¹⁷. Addition of another metal has been attempted to modify the Pd catalytic and selectivity properties to account for both the electronic and geometric effects brought about by the creation of rearrangements¹⁸⁻¹⁹. Zn inclusion probes the ability to have specific Pd_n active site ensembles, since Zn is inactive diluent. The use of PdZn-based catalysts had been explored because it has shown good selectivity and stability for different reactions ^{16, 19-21}.

An earlier study²² reported the high stability of phase β_1 -PdZn alloys based on the observed critical transition temperature of 4546 K and a highly exothermic Gibbs free energy of formation of -12 kcal/g atom at 1273 K. They attributed the high stability of this phase to the transfer of electrons from zinc to the *d*-band of palladium. PdZn was proven to exhibit a similar valence electron density of states as pure Cu based on energy band calculation and X-ray photoelectron spectroscopy²³. They showed that an intermetallic compound may be designed by band structure calculation wherein a selected metallic element was changed without changing the catalytic function. Using the intermetallic compound PdGa as a catalyst for the selective hydrogenation of acetylene to ethylene, the concept that involved the use of well-defined, ordered and in situ stable unsupported intermetallic compounds to circumvent the problems brought about by the presence of a variety of active sites, their possible agglomeration, metal-support interactions and segregation of the components was demonstrated²⁴.

1.2.1. Discovering and predicting performance of intermetallic catalysts: density functional theory (DFT)

Experimental studies applied in the search for new catalyst with specific desired characteristics, such as high activity and good selectivity, potential for industrial-scale applications, and a multitude of other important requirements require considerable resources and cannot keep pace with the accelerating studies of intermetallics^{25, 26}. Computational techniques, such as DFT, have been widely used to facilitate screening and selection of predictively higher-performing catalysts²⁵⁻²⁷. This allows for atomistic pictures of catalysts with specific atom positions being able to be identified, manipulated, and utilized for catalytic reactions. For example, Krajci and Hafner (2016)²⁸ noted that DFT was useful in the development of an atomistic picture of the catalytic properties of intermetallic compounds in the semi-hydrogenation of acetylene,

steam reforming of methanol, and identification of Zn-Pd and Ga-Pd compounds as active and selective catalysts. Rankin and Waldt (2019)²⁷ applied DFT computations across a suite of ternary Pt-based intermetallic alloys with both intermetallic and Pt-skin and Pt-subsurface layer structure(s) to predictively identify higher-performance, lower-cost oxygen reduction reaction technologies. A combined experimental and DFT-calculated study conducted by Purdy et al. (2020)²⁹ allowed for the synthesis of a series of Pd alloy catalysts with five promoters: In, Zn, Ga, Fe, and Mn; it was shown that the DFT calculated trends were fully consistent with the experimental results.

Our research group has likewise been using a combination of experimental and computational methods to examine various bulk intermetallics. Pd-M-Zn (M = Pd, Cu, Ag, Au, Zn) γ -brass phase intermetallic catalysts have been studied to examine the selective hydrogenation of acetylene and ethylene³⁰, which was a basis for this thesis. Similarly, Ni-Ga catalysts have also been studied for acetylene selective hydrogenation in ethylene³¹. The group had also previously studied Ni-Zn catalysts γ -brass³²⁻³³.

1.3. Conclusions

Advances have been achieved in investigating the potential of using intermetallics in heterogenous catalysis. There are continuing research and development work to discover technologies and methodologies that will help address current limitations. Different approaches and ideas have been investigated for specific targets that may vary for the many potential applications. With the enormous contribution of catalysis for a wide range of applications that are critical in providing for a clean and safe environment, sustainable energy infrastructure (petroleum industry, polymer synthesis, hydrogen production, etc.), and reliant food source, among others, it is expected that there will be continuing and further investment in resources towards a better understanding and improvement in harnessing the potential of intermetallic compounds for catalysis.

The current study seeks to contribute further to the knowledge base that relates to the utilization of the Pd-Zn based γ -brass phase as a model catalyst, which is covered in Chapter 2, and the examination of possible higher Pd content active sites as shown in Chapter 3. The recommendations for further research are summarized in Chapter 4.

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CHAPTER 2 Utilizing the Pd-Zn based γ-brass phase as a model catalyst

2.1. Introduction

The Pd-Zn γ -brass phase (I $\overline{4}$ 3m) has been utilized in selective catalysis for its ability to precisely control active site ensembles (specific shape/clustering of Pd active metals on a surface) through small changes in stoichiometry¹. The γ -brass phase is in the Zn rich composition of the Pd-Zn phase diagram (Figure 2.1) and is comprised of 52 atoms per unit cell for Pd_xZn_{52-x} catalysts. The γ -brass unit cell is comprised of 26 interpenetrating BCC unit cells, with four unique symmetry sites, comprised of outer tetrahedral (OT), inner tetrahedral (IT), octahedral (OH), and cuboctahedral (CO), which form two sets of nested polyhedra (at the origin and center of the unit cell)¹³. Figure 2.2a depicts one of these two polyhedra.



Figure 2.1. Phase diagram of palladium zinc (*Source: Predel, 1988*²) highlighting γ brass phase (encircled in red).



Figure 2.2. Models of (a) the sites of the γ -brass unit cell (OT = blue, IT = red, OH = green, CO = orange), and the $1\overline{10}$ surface of (b) Pd₈Zn₄₄ (x = 8), (c) Pd₉Zn₄₃ (x = 9), and (d) Pd₁₀Zn₄₂ (x = 10), where gray atoms are Zn and blue atoms are Pd or M (*Source: Dasgupta et al., 2019³*).

The γ -brass phase is a Hume-Rothery phase, in which crystal structure is determined based on the valence electron concentration (VEC). When considering concentrations of Pd that is possible for a Pd-Zn γ -brass using VEC values, Pd₈Zn₄₄ had the lowest thermodynamically favored amount of Pd, and while Pd₁₁Zn₄₁ is possible, a distorted orthorhombic super structure was observed⁴. The cubic phases of the Pd-Zn γ -brass phase have been the focus in our research group⁵.

In Pd-Zn γ -brass, active sites of Pd are isolated in Zn, which can have varying nuclearity. Through the use of density functional theory (DFT), it has been identified that on the lowest energy (most stable) {110} surface of the γ -brass structure, with tuning amounts of Pd in Pd_x-M-Zn_{52-x}, different active sites appear (Figure 2.2b-d)⁵. For x = 8, isolated monomer active sites appear and with the increasing Pd content (8 < x ≤ 10) is an increase in trimer sites.

The unique change in nuclearity with small changes in composition of the γ -brass structure has allowed the phase to be utilized as a tunable active site for acetylene semi-hydrogenation and ethylene hydrogenation⁶. The monomer sites of the Pd₈Zn₄₄ surface is highly selective towards acetylene semi-hydrogenation but low activity occurs. On the other hand, the trimer sites of the Pd₉Zn₄₃ and Pd₁₀Zn₄₂ surfaces exhibit low selectivity towards acetylene semi-hydrogenation but there is high activity.

This behavior probes the desire to further study the γ -brass active site. First, we evaluated the effects of using the trimer active site for propylene hydrogenation with comparison to ethylene

hydrogenation. We then studied the trimer site utilizing a ternary coinage metal (Cu, Au, or Ag), where it had been previously shown to be useful in understanding the selectivity-activity trade-off of the semi-hydrogenation of acetylene in the presence of ethylene.

2.2. Ethylene vs. propylene hydrogenation

Acetylene semi-hydrogenation in the presence of ethylene is a commercially important reaction for the process of polymerization of ethylene. The presence of acetylene in the feed stream can lead to deactivation of the polymerization catalyst⁷. Thus, it is important to minimize the presence of the acetylene, where the hydrogenation of acetylene to ethylene is an optimal solution. However, it must be ensured that the hydrogenation of acetylene leads to little or no hydrogenation of ethylene to ethane (Figure 2.3). Previous studies have shown that the Pd-Zn γ -brass phase is a possible catalyst to be used for this reaction⁶.



Figure 2.3. Hydrogenation pathway of acetylene to ethane, where the hydrogenation of ethylene to ethane is not desired.

When studying the selectivity of this catalyst, to simulate an industrial feed stock, acetylene and isotopically labeled ethylene are co-fed to a flow reactor with hydrogen. A mass spectrometer is required in the analysis of the resulting ethylene and ethane to understand if the products resulted from the hydrogenation of acetylene or ethylene. The use of isotopically labeled ethylene is expensive and a cheaper alternative is desired. The use of propylene in place of ethylene was investigated to determine the potential as a possible surrogate for co-fed experiments of acetylene and ethylene. A comparison between propylene and ethylene was performed using DFT through adsorption energies and activation barriers of the two molecules to the $Pd_9Zn_{43} \gamma$ -brass surface.

2.2.1. Computational methods

Structure optimization calculations were performed using DFT with the Vienna Ab Initio Simulation Package (VASP). The Perdew-Burke-Ernzerhoff (PBE) generalized gradient approximation was used with a plane wave basis set with a cutoff energy of 450 eV. The Monkhorst-Pack k-point mesh of 6x6x1 for all surface structure optimization of all phases was analyzed. The Monkhorst-Pack k-point mesh was optimized for each surface studied. The Methfessel-Paxton (MP) smearing method with 0.2 eV broadening value was utilized.

2.2.2. Results and discussion

2.2.2.1 Ethylene vs. propylene adsorption to the surface.

To first understand the possibility of using propylene as a surrogate in labeled ethylene experiments, a comparison of the adsorption of ethylene and propylene to the Pd_8Zn_{44} and Pd_9Zn_{43} catalysts were studied. Single molecules of ethylene or propylene were adsorbed to the Pd_8Zn_{44} or Pd_9Zn_{43} surfaces and the optimization calculations were performed. Figure 2.4 shows the adsorption configurations of ethylene and propylene to the surfaces. Figures 2.4a and b depict ethylene and propylene adsorption onto the Pd_8Zn_{44} surface, where adsorbates bind with their double bond over an atop Pd_1 site. The adsorption of propylene has no preferential rotational orientation (relative to the surface normal), making rotational orientation unimportant in altering the adsorption energy. Figures 2.4c to e show the adsorption of ethylene and propylene to the surface. For the Pd_9Zn_{43} structure, the location of the additional methyl group on the propylene is

examined with its location being towards (d) or away (e) from the Pd₃ trimer. The configuration with the methyl group towards the trimer is denoted as Propylene_C1, and the propylene with the methyl group away as Propylene_C2.







(b)



(c)





Figure 2.4. Configurations of (a) ethylene on Pd₈Zn₄₄, (b) propylene on Pd₈Zn₄₄, (c) ethylene on Pd₉Zn₄₃, (d) propylene_C1 on Pd₉Zn₄₃, and (e) propylene_C2 on Pd₉Zn₄₃.

Tables 2.1 and 2.2 show the adsorption energies for ethylene and propylene on the Pd₈Zn₄₄ and Pd₉Zn₄₃ surfaces, respectively. Two calculations of each were performed, with and without van der Waals (VDW) forces, to understand if VDW interactions between atoms and the adsorbates to the surface are important to the relative adsorption energies. Between the Pd₈Zn₄₄ and Pd₉Zn₄₃ surfaces, the ethylene and propylene adsorbed similarly to each surface. When VDW forces were not considered, it was observed that ethylene adsorption was more favorable to both Pd₈Zn₄₄ and Pd₉Zn₄₃. Additionally, comparison of the adsorption of propylene_C1 and propylene_C2 showed that without VDW forces, configuration to the surface had noticeable differences in adsorption. VDW forces are often neglected in small molecule adsorption but are seen to be important for these C2 and C3 adsorbates⁸. With the consideration of VDW forces, propylene and ethylene adsorbed similarly to the surface. Thus, based on adsorption energies, we believe propylene may be a candidate as a surrogate for this reaction.

	Adsorption Energy No VDW (eV)	Adsorption Energy VDW (eV)
Ethylene	-0.34	-0.81
Propylene	-0.20	-0.88

Table 2.1. Adsorption energies of ethylene and propylene on Pd₈Zn₄₄.

Table 2.2. Adsorption energies of ethylene and pr	opvlene on Pd ₉ 2	Zn_{43} .
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	Adsorption Energy No VDW (eV)	Adsorption Energy VDW (eV)
Ethylene	-0.34	-0.83
Propylene_C1	-0.22	-0.87
Propylene_C2	-0.13	-0.82

2.2.2.2. Diffusion of hydrogen and first hydrogenation step activation barriers

Activation barriers are utilized to help understand reaction mechanisms and their limiting steps. Through previously calculated results, it was observed that the overall hydrogenation of an alkene happens in two steps. With the molecule on one Pd atom, the hydrogen adsorbed on the opposite Pd in the trimer first diffuses over the trimer site to in-between the center Pd and the Pd with adsorbed the molecule; this was followed by the hydrogenation of the molecule⁶.

Through DFT, activation barriers of hydrogen diffusion and the first hydrogenation step were calculated for ethylene and two configurations of propylene on the Pd₉Zn₄₃ surface for use in comparison of how they would act under desired reaction. The Pd₉Zn₄₃ surface was utilized as ethylene does not hydrogenate on the Pd₈Zn₄₄ surface. Calculations of these activation barriers were performed with both VDW forces turned off and on. Figure 2.5 shows the energy profiles and activation barriers for this reaction.

Based on the results of the first activation barrier related to the diffusion of hydrogen over the trimer active site, it is shown that for ethylene and propylene_C1, the barriers were similar for calculations with and without VDW forces. However, the barriers differed substantially for propylene_C2. It was hypothesized that there are at least two possible paths that hydrogen may take during diffusion, resulting in one of two possible activation energies. For the first hydrogenation activation barrier (the 2nd barrier), ethylene and propylene_C1 had similar barriers. Propylene_C2 was shown to have a higher activation barrier compared to the other adsorbates, and thus was less favorable or less likely to occur. Therefore, it was predicted that ethylene and propylene_C1 may hydrogenate similarly to one another for the Pd₉Zn₄₃ surface, but that the substitution of a methyl group has a small effect on the secondary C hydrogenation barrier. For the purpose of this study, it was hypothesized that the first hydrogenation step activation barrier will predict the possibility for reaction, therefore the differences in the diffusion barriers will be bypassed.



Figure 2.5. The energy profiles and activation barriers of hydrogen diffusion (E_{A1}) and first hydrogenation step (E_{A2}) for (a) ethylene with no van der Waals forces, (b) ethylene with van der Waals forces, (c) propylene_C1 with no van der Waals forces, (d) propylene_C1 with van der Waals forces, (e) propylene_C2 with no van der Waals forces, and (f) propylene_C2 with van der Waals forces.

2.2.3. Conclusions

The possible uses of propylene in place of ethylene for co-fed acetylene experiments were determined through DFT calculations to compare the adsorption, reaction, and activation energies. Both ethylene and propylene exhibited similar results in terms of initial adsorption of the molecule when applying VDW interactions. When observing similarities through activation energies, ethylene and propylene_C1 resulted in similar hydrogen diffusion barriers. The propylene_C1 configuration also exhibited similar hydrogenation activation barriers to that of the ethylene barrier, with the hydrogenation barrier of propylene_C2 being higher. This would suggest that hydrogenation through the first carbon is more favorable to occur first. Additionally, propylene_C1 showed similar behavior to that of ethylene. Thus, the possibility of using propylene in place of ethylene is computationally confirmed to be possible.

2.3. Synthesis and characterization of ternary Pd-M-Zn γ-brass catalysts

Binary Pd-Zn γ -brass phases are useful for their active site specifications towards acetylene semi-hydrogenation. The monomer active site of Pd₈Zn₄₄ results in acetylene semi-hydrogenation being highly selective but having low activity (conversion). In comparison, higher Pd content catalysts with trimer active sites (Pd₉Zn₄₃ and Pd₁₀Zn₄₂) exhibited low selectivity to acetylene semi-hydrogenation, but higher activity, thus showing a trade-off in reactivity. The introduction of a ternary metal into the γ -brass (Pd-M-Zn where M = Pd, Cu, Au, or Ag) is able to "fill-in" this gap in reactivity, as shown in Figure 2.6a. The use of DFT and Rietveld Refinement using GSAS software of powder X-ray and neutron diffractograms were studied to observe the effect/location of the ternary metal to the active site¹⁰. The ternary metal will occupy an OH site, where on the lowest energy facet is the center atom of the trimer, as shown in Figure 2.6b.



Figure 2.6. Previous results of ternary γ -brass catalysts through (a) its role in "filling" the activityselectivity trade-off of binary γ -brass catalysts and (b) the DFT and Rietveld refinement discovered location of the ternary (M) metal. (*Source: Dasgupta, 2019*⁴)

Pd-M-Zn (M = Pd, Cu, Au, Ag) γ -brass catalysts were synthesized and characterized with the intention of being used to understand the active site requirements for the probe reaction of ethylene (discussed further in Section 4.2.1). Four Pd-M-Zn catalysts were synthesized with the following stoichiometries: Pd₉Zn₄₃, Pd₉CuZn₄₃, Pd₉AuZn₄₃, Pd₉AgZn₄₃. These catalysts were characterized through elemental analysis with ICP-OES, phase identification through powder Xray diffraction, and Rietveld refinement of the diffractograms to better understand locations and occupancies of atoms through the four symmetry non-equivalent sites in the γ -brass structure.

2.3.1. Experimental methods

2.3.1.1. Synthesis of Pd-M-Zn catalysts

Pd-M-Zn catalyst samples (M = Pd, Cu, Au, Ag) with the γ -brass structure were synthesized with stoichiometries of Pd₉Zn₄₃, Pd₉CuZn₄₃, Pd₉AuZn₄₃, Pd₉AgZn₄₃. Pd powder (Sigma Aldrich), Zn powder (Sigma Aldrich), and the ternary metal (Cu) granules (Sigma Aldrich), Au powder (Sigma Aldrich), or Ag powder (Strem Chemicals), were added stoichiometrically to alumina crucibles (LSP Ceramics, 13 mm ID). The samples were evacuated to ~60 mTorr and flame-sealed in quartz ampoules. Samples were synthesized through solid state diffusion where they were heated in a box furnace to 800°C for over 20 hours, held at 800°C for 92 hours, cooled to 500°C for over 8 hours, then cooled to room temperature. The sample ingots were extracted from the crucibles, then were milled to powder with 4 mL of 1,1,1,2,2,3,4,5,5,5 decafluoropentane (Vertrel XF, Dupont) as the fluidizing agent using a ball mill (SPEX SamplePrep 8000D Mixer/Mill with 8001 Grinding Vial) in an air-free (N₂) environment. Samples were unloaded from ball mill containers in an air-free (N₂) glove box to allow for the Vertrel XF to evaporate at room temperature. The resulting powders were then annealed in evacuated quartz ampoules at 500°C for 168 hours to ensure samples are in their thermodynamically preferred arrangement.

2.3.1.2. X-ray diffraction (XRD)

X-ray diffraction (XRD) was performed using a PANalytical Empyrean diffractometer using constant wavelength Cu K_{α} radiation, utilizing a 2 θ range of 10-90°, to examine the phases present in our catalysts. The optics of the incident side had 1/2° anti-scatter, 1/4° fixed divergence, and 0.04 rad soller slits and a 10 mm beam mask. The detector side was outfitted with a PixCel detector with 1/2° anti-scatter and 0.04 rad soller slits, and a Ni- β filter to suppress Cu K_{β} radiation. Each sample was placed on a silicon zero-background holder to eliminate background signal. The resulting diffractogram was analyzed using Materials Data JADE for phase identification.

2.3.1.3.Rietveld refinement

Rietveld refinement was performed using the Materials Data JADE software's whole pattern fitting + Rietveld feature. Utilizing diffractograms obtained from XRD, models were refined to the pattern, determining which model would best represent the catalyst. The JADE software allows for occupancy factors to be adjusted for any symmetrically inequivalent site. In the γ -brass structure, it had been earlier noted that there are four symmetrically inequivalent sites per unit cell (Section 2.1). Several models were made for each catalyst referencing site occupancies based on results from Dasgupta et al.⁴

Data was initially fitted with the occupancies of the γ-brass structure from Dasgupta et al.⁹. Utilizing ICP-OES values, the occupancies were then calculated and fitted to the data. From there, models were developed with adjusting occupancies of Pd and Zn and M and Zn for each catalyst to find the occupancies that would result in the best fit. Several simplifications were verified and utilized from their study, which were utilized in this study: (1) Zn does not refine to the OT site^{9,10}, (2) Pd and M do not refine to the CO or IT sites, (3) M also does not refine to OT sites, and (4) all elements can refine to the OH site⁹.

The background of the pattern was estimated using a refinable polynomial background (adjusted for each pattern). The full width half max (FWHM) for the pattern was determined within the program and was used as a parameter to calculate the profile shape function (PSF) or the shape of the curve using the pseudo-Voigt approximation. Models were compared based on factors calculated in the JADE software: the agreement factor of weighted value (R) and goodness of fit (R/E), where values of R < 10% and R/E \approx 1.0 would indicate the best fit and atom locations within the unit cell.

2.3.1.4. Elemental analysis of Pd-M-Zn catalysts using ICP-OES

Inductively coupled plasma optical emission spectrometry (ICP-OES) using an Agilent Technologies 700 series ICP-OES was utilized to determine the average composition of the Pd-M-Zn catalysts. The ICP-OES was calibrated using solutions of various concentrations of Pd, Cu, Au, Ag, and Zn (1 mg/mL, High Purity Standards), diluting with DI water to 16 mL total. 10 mg of each sample was dissolved in 4 mL of aqua regia, then diluted to 16 mL with DI water. Each calibration and catalyst sample contained 20 μ L of Indium (1 mg/mL, High Purity Standards) as an internal standard.

2.3.2. Results and discussion

2.3.2.1.Phase identification - XRD and Rietveld refinement

Diffractograms from the powder x-ray diffraction of the Pd₉Zn₄₃, Pd₉CuZn₄₃, Pd₉AuZn₄₃, Pd₉AgZn₄₃ samples are shown in Figure 2.7. Each sample has peaks indexed to that of the γ -brass crystal structure, the desired structure. The samples also have two peaks at 20 of 25.5° and 31.6°, which may be attributed to an unidentified impurity; this has not been identified from all possible elements utilized and other common impurities. The Pd₉Zn₄₃ additionally has small intensity peaks indexed to zinc oxide (ZnO, P63mc) at 20 of 36.2°.



Figure 2.7. X-ray diffraction pattern data of Pd₉Zn₄₃ (black), Pd₉CuZn₄₂ (red), Pd₉AuZn₄₂ (green) and Pd₉AgZn₄₂ (blue).

The resulting best fitting Rietveld refinement data is shown in Table 2.3. Through confirmation model testing, simplifications listed above in terms of allowed occupancies of each site were deemed correct, therefore models were tested through changes of occupancies of the OH site.

Correlating with ICP-OES results, it was observed that slight additional Pd is desired for best refinement fit to the diffraction data. Additionally, all ternary metals had occupancies that agreed with the objective of having a single ternary element in the molecule stoichiometry that only occupied the OH site. These results were consistent with the results of Dasgupta et al.⁴ confirming that the trimer site of the γ -brass structure is occupied by only Pd or M atoms (where Zn occupancy would result in monomer active sites). The results also agreed with their results as the ternary metal desires to only occupy OH sites, and therefore is the center atom of the trimer site.

Data may not reflect exact occupancies of the OH site. JADE software contains a limitation to which it will only test fit to the specific occupancies provided to it, rather than actively changing occupancies to best fit the x-ray diffraction data.

Site ^a	Element	Parameter	Pd ₉ Zn ₄₃	Pd ₉ CuZn ₄₂	Pd ₉ AuZn ₄₂	Pd ₉ AgZn ₄₂ ^b
		a (Å)	9.105	9.095	9.118	9.119
		R (%)	9.08	8.26	6.58	7.75
		R/E	3.06	2.82	2.31	2.60
IT (8)	Zn	SOF	1	1	1	1
OT (8)	Pd	SOF	1	1	1	1
OH (12)	Pd	SOF	0.148	0.118	0.108	0.175
	М	SOF	0	0.091	0.085	0.07
	Zn	SOF	0.852	0.791	0.807	0.755
CO (24)	Zn	SOF	1	1	1	1

Table 2.3. Fit parameters, fractional coordinates, and site occupation factors (SOF) from refinement of Pd₉Zn₄₃, Pd₉CuZn₄₃, Pd₉AuZn₄₃, Pd₉AgZn₄₃ γ-brass catalyst.

^a Quantities in parenthesis represent the multiplicity of each site in the unit cell.

^b No differentiation between Pd and Ag is possible due to identical x-ray scattering cross sections, therefore SOF proportions of Pd and M are not easily differentiated/may not be correct

2.3.2.2. ICP-OES

ICP-OES results showed the composition of the synthesized γ -brass catalysts (Table 2.4). The material composition of all materials was found to be close to that of the intended compositions. While all samples were slightly Pd rich, all samples were within the γ -brass composition range and were further confirmed to be that of the intended phase through the XRD results.

Sample	ICP Composition
Pd ₉ Zn ₄₃	Pd _{9.46} Zn _{42.54}
Pd ₉ CuZn ₄₂	Pd _{9.41} Cu _{1.17} Zn _{41.42}
Pd ₉ AuZn ₄₂	Pd9.30Au0.89Zn41.80
Pd ₉ AgZn ₄₂	Pd9.37Ag0.84Zn41.78

Table 2.4. ICP-OES elemental analysis of Pd-M-Zn catalysts.

2.3.3. Conclusions

Ternary γ -brass catalysts of compositions of Pd₉Zn₄₃, Pd₉CuZn₄₂, Pd₉AuZn₄₂, and Pd₉AgZn₄₂ were synthesized through solid state diffusion. This was confirmed through the combined usage of X-ray diffraction, Rietveld refinement, and elemental analysis with ICP-OES. X-ray diffraction data confirmed the synthesized phase of the catalysts were that of the γ -brass phase. Diffraction had also identified an unknown impurity within the catalyst. Rietveld refinement was performed to understand the occupancies of each element to the different sites of the γ -brass structure. It had been found that the OT site is only occupied by Pd, the IT and CO sites by Zn, and the OH site that can be occupied by all three elements. It was found that best fitting results were found with data close to that of the ICP-OES stoichiometric data. Therefore, it is confirmed that ternary γ -brass catalysts were synthesized. These catalysts will eventually be used for catalytic testing with ethylene hydrogenation, which will be discussed further in Section 4.2.1.

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CHAPTER 3 β1 phase Pd-Zn to examine possible higher Pd content active sites

3.1. Introduction

Earlier research focused on the γ -brass intermetallic phase, which is in the Zn rich region of the Pd-Zn periodic table. The β_1 is used to explore a phase that allows for compositional tuning in the Pd rich region of the phase diagram. The β_1 phase (space group: P4/mmm or I4/mmm) is a tetragonal intermetallic crystal structure of Pd-Zn. The phase is located at the center of the Pd-Zn periodic table, containing PdZn (nominally Pd₁Zn₁) and both Pd and Zn rich compositions (Figure 3.1). The Pd₁Zn₁ unit cell is body centered, with Zn centrally located in the unit cell (Figure 3.2).



Figure 3.1. Phase diagram of palladium zinc (Source: Predel, 1988¹) highlighting β_1 phase (encircled in red).



Figure 3.2. The PdZn β_1 unit cell.

The β_1 phase has been utilized for several chemistries such as methanol reforming¹⁻³, propane dehydrogenation⁴, and acetylene semi-hydrogenation⁵. The intermetallic compound, PdZn, was shown to have catalytic function that was solely governed by the valence band structure of the catalyst was identical to that of Cu, which explains the high selectivity of PdZn for the steam reforming of methanol². Based on this, they suggested that intermetallic compounds can be logically designed by band structure calculation. The intermetallic alloying of one active metal with another inert component to form an ordered crystal structure promoted the dispersion of active sites with single atom distribution and provided a unique and homogenous ensemble of active sites that can serve as adaptive sites for different catalytic processes⁵. They showed that PdZn intermetallic nanostructure with Pd-Zn-Pd ensembles are both highly reactive and selective for semi-hydrogenation of acetylene to ethylene, which is usually inaccessible due to the sequential hydrogenation to ethane. Based on experimental characterizations and density functional theory (DFT), they showed that appropriate spatial arrangement of Pd sites in the Pd-Zn-Pd ensembles of the PdZn alloy restrained the chemisorption of ethylene while the absorption toward acetylene and the activation of hydrogen was facilitated. The formation of β -PdZn alloys has been reported where the effect on the mechanism of reaction was attributed to geometric modifications that

changed the ensemble of active atoms³. Based on X-ray diffraction and in conjunction with *in-situ* diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS), the β_1 -PdZn intermetallic alloy structure was formed first at the surface at reduction temperatures as low as 230 °C with DRIFTS results suggesting that there was little change in the surfaces of the nanoparticles above $325^{\circ}C^{4}$. They noted based on *in situ* extended X-ray absorption fine structure that there was extensive formation throughout the bulk only when it reached 500°C. Also noted was that the intermetallic alloy which formed was Pd-rich at all temperatures but became less Pd-rich with increasing reduction temperature as more Zn was incorporated into the structure.

These studies utilize 1:1 PdZn and did not explore the different compositions of the β_1 phase further. While both Pd- and Zn-rich structures exist in this phase, our design is to examine Pd-rich structures to determine whether distinct Pd_n ensembles can be prepared as previously demonstrated with Pd addition to the Zn-rich γ -brass phase. Several possible β_1 phase structures (Pd₉Zn₇ and various Pd₁₀Zn₆) structures are constructed through the substitution of Pd in Zn locations (Figure 3.3).

3.2. Computational methods

Structure optimization calculations were performed using DFT with the Vienna Ab Initio Simulation Package (VASP). Perdew-Burke-Ernzerhoff (PBE) generalized gradient approximation was used with a plane wave basis set with a cutoff energy of 450 eV. The Monkhorst-Pack k-point mesh of 6x6x6 for bulk structures and 6x6x1 for all surface structure optimization of all phases were analyzed. The Monkhorst-Pack k-point mesh was optimized for each surface studied. The Methfessel-Paxton (MP) smearing method with 0.2 eV broadening value was utilized.



Figure 3.3. Bulk unit cell structures of high Pd content β_1 phase and their inner atom arrangements of (a) Pd₁₀Zn₆_1, (b) Pd₁₀Zn₆_2, (c) Pd₁₀Zn₆_3, and (d) Pd₉Zn₇.

3.3. Results and discussion

Low index facets (no Miller index greater than 1) were cut from the optimized bulk structures of the β_1 phase. The facets revealed a variety of possible active site nuclearities, where the surfaces resulted in stoichiometric (the number of atoms in the surface slab is a multiple of that of the bulk) and non-stoichiometric (number of atoms in the surface slab does not match that of the bulk) surfaces. Table 3.1 shows the five resulting facets for stoichiometric and nonstoichiometric surfaces of Pd₁₀Zn₆ and Pd₉Zn₇.

To better understand what surface may be most likely to result from a certain composition, surface energies must be calculated and compared. However, with resulting slabs that are both stoichiometric and non-stoichiometric, calculating surface energies for comparison becomes much less trivial.

3.3.1. Stoichiometric surface energies

Stoichiometric surfaces are surfaces where the number of atoms in the facet are equivalent to a multiple of the number of atoms in the bulk surface. Surface energies for stoichiometric facets can simply be calculated with the equation (1) below.

$$Surface Energy = \frac{E_{DFT \, Calc} - nE_{Bulk}}{2A} \tag{1}$$

where $E_{DFT-calc}$ represents the energy of the surface slab, nE_{bulk} is the energy of the referenced bulk Pd-Zn energy with the same stoichiometry, and 2A is the total area of the top and bottom surfaces in the slab model. Energies of the specific surface and the bulk unit cell energy are used to calculate the specific surface energy. This allows for direct comparison of surfaces, as surfaces are normalized using the area of the surface. Table 3.2 shows each of the stoichiometric surface energies, where all surfaces resulted in active sites with the Pd atoms arranged in an "X" ensemble (Table 3.1).

While all possible surface facets had relatively similar surface energies, the $Pd_{10}Zn_{6}1$ 101 and $Pd_{10}Zn_{6}2$ 011 facets were found to have the lowest surface energy, thus the most stable and most likely surface to exist for all stoichiometric surfaces. No $Pd_{9}Zn_{7}$ surfaces resulted in a stoichiometric surface.

Surface Image	Ensemble	Facets
	Х	$\begin{array}{c} Pd_{10}Zn_{6}_1 \ 101\\ Pd_{10}Zn_{6}_1 \ 110\\ Pd_{10}Zn_{6}_2 \ 110\\ Pd_{10}Zn_{6}_2 \ 011\\ Pd_{10}Zn_{6}_2 \ 001\\ Pd_{10}Zn_{6}_3 \ 011\\ Pd_{9}Zn_{7} \ 011\\ Pd_{9}Zn_{7} \ 110\\ \end{array}$
	Triple	Pd ₁₀ Zn ₆ _1 011
	Off-set monomers	Pd ₁₀ Zn ₆ _2 101 Pd ₁₀ Zn ₆ _3 101 Pd ₉ Zn ₇ 101
	In-line monomers	Pd ₁₀ Zn ₆ _1 001
	Boxed	$\begin{array}{c} Pd_{10}Zn_{6}_2 \ 001 \\ Pd_{10}Zn_{6}_3 \ 001 \\ Pd_{10}Zn_{6}_3 \ 001 \\ Pd_{10}Zn_{6}_3 \ 010 \end{array}$

Table 3.1. All possible active site ensembles, their ensemble names, and
possible facets for the β_1 phase.

Surface Facet	Surface Energy (eV/ Å ²)
Pd ₁₀ Zn ₆ _1 101	0.075
Pd ₁₀ Zn ₆ _1 110	0.078
Pd ₁₀ Zn ₆ _2 110	0.076
Pd ₁₀ Zn ₆ _2 011	0.075

Table 3.2. Surface energies for all stoichiometric β_1 phase structures.

3.3.2. Non-stoichiometric surface energies

Non-stoichiometric surfaces are surfaces where the number of Pd and Zn atoms in the surface slab are not a direct multiple of that in a reference bulk Pd-Zn structure. Unlike stoichiometric surfaces, when calculating surface energies, we cannot simply reference the bulk energy as no value of n for equation (1) will allow for the chemical formula of the surface and the bulk to be equivalent. Thus, different references must be utilized to calculate the surface energy of each non-stoichiometric surface, invoking a "reservoir" of excess Pd or Zn atoms from which to draw to balance the slab and bulk reference stoichiometries. Calculations are performed using the equation (2) below:

$$Surface Energy = \frac{E_{DFT \ Calc} - nE_{Pd_{10}Zn_6/Pd_9Zn_7/PdZn} - mE_{Pd/Zn}}{2A}$$
(2)

Several references can be utilized in the calculation of non-stoichiometric surface energies. Thus, several references were utilized for various surface energies for a single surface. Tables 3.3 to 3.6 show the various surface energies of all non-stoichiometric surfaces for $Pd_{10}Zn_6$ and Pd_9Zn_7 .

References	011 Facet (eV/ Å ²)	001 Facet (eV/ Å ²)
$Pd_{10}Zn_6$ and Pd	0.071	0.099
PdZn and Pd	0.048	0.085
$Pd_{10}Zn_6$ and Zn	0.070	0.099
PdZn and Zn	0.028	0.077

 Table 3.3. Surface energies of the Pd₁₀Zn₆_1 non-stoichiometric facet (011) utilizing different references.

Table 3.4. Surface energies of the $Pd_{10}Zn_{6}_{2}$ non-stoichiometricfacets (101 and 001) utilizing different references.

References	101 Facet (eV/ Å ²)	011 Facet (eV/ Å ²)
$Pd_{10}Zn_6$ and Pd	0.079	0.102
PdZn and Pd	0.055	0.082
$Pd_{10}Zn_6$ and Zn	0.080	0.103
PdZn and Zn	0.039	0.074

Table 3.5. Surface energies of the Pd₁₀Zn₆_3 non-stoichiometric facets (110, 011, 101, 010, and 001) utilizing different references.

References	110 Facet (eV/ Å ²)	011 Facet (eV/ Å ²)	101 Facet (eV/ Å ²)	010 Facet (eV/ Å ²)	001 Facet (eV/ Å ²)
$Pd_{10}Zn_6$ and Pd	0.098	0.070	0.081	0.097	0.099
PdZn and Pd	0.074	0.048	0.056	0.079	0.078
Pd ₁₀ Zn ₆ and Zn	0.098	0.070	0.081	0.096	0.099
PdZn and Zn	0.050	0.027	0.041	0.088	0.070

Table 3.6. Surface energies of the Pd₉Zn₇ non-stoichiometric facets (101, 011, and 110) utilizing different references.

References	101 Facet (eV/ Å ²)	011 Facet (eV/ Å ²)	110 Facet (eV/ $Å^2$)
Pd ₉ Zn ₇ and Pd	0.103	0.069	0.055
PdZn and Pd	0.085	0.051	0.037
Pd ₉ Zn ₇ and Zn	0.102	0.078	0.055
PdZn and Zn	0.074	0.059	0.030

Based on the varying surface energies, it is difficult to definitively select which surface would be most stable. Surface energies for each facet have the possibility of having a large range of possible surface energies and knowing which specific reference may be considered the most relevant to represent experimental conditions is not determinable. However, if we compare data between stoichiometric and non-stoichiometric surface energies, the $Pd_{10}Zn_{6-1}$ 011 and $Pd_{10}Zn_{6-3}$ 011 facets have lower surface energies for each facet compared to the lowest surface energies of the stoichiometric $Pd_{10}Zn_{6-1}$ 101 and $Pd_{10}Zn_{6-2}$ 011 facets. The $Pd_{10}Zn_{6-1}$ 011 facet had the "triple" ensemble and the $Pd_{10}Zn_{6-3}$ 011 facet had the "X" ensemble. Between each other, the energies were quite similar, therefore it is not easily determinable if the "triple" or "X" ensemble would more likely appear.

When considering the Pd₉Zn₇, the three facets (101, 011, and 110) result in two possible active site ensembles, "off-set monomers" and "X". All three facets have energies that overlap the ranges of the other facets. Therefore, since we cannot determine which reference would be correct, it cannot easily be said which active site ensemble would be most stable.

3.3.3. Surface stability through surface exchange calculations

Though the Pd "X" configuration may be an interesting active site ensemble and results from cutting specific facets of the bulk structures considered, we have to further examine whether such ensembles are stable relative to rearrangements of Pd and Zn atoms in the surface slab. Surface exchange energies were calculated to determine the stability of the active site of the optimized facets of the β_1 phase. Surface atom positions were exchanged, disrupting existing nuclearity, and DFT optimization calculations were done. The resulting energy ($E_{exchanged}$) and the previously optimized energy ($E_{Original}$) were used to calculate the change in energy ($\Delta E = E_{exchanged}$) - $E_{Original}$) to understand stability. ΔE values that are positive suggest that the original structure is more stable than that of the structure where the surface atoms are exchanged. Original and exchanged surfaces are shown in Table 3.7. A surface exchange area is not calculated for the "boxed" active site ensemble; when performing surface exchanges on this surface, the active site ensemble is only shifted across the surface which is similar to that of Table 3.7b.

Facet and Ensemble	Before Exchange	After Exchange	ΔE (eV)
(a) Pd10Zn6_1 101 "X"			0.47 eV
(b) Pd10Zn6_1 101 "X"			-0.09 eV
(c) Pd10Zn6_1 011 "Triple"			0.55 eV
(d) Pd10Zn6 – 2 101 "Off-set monomers"			0.68 eV
(e) Pd10Zn6_1 001 "In-line monomers"			-0.49 eV

Table 3.7. Surface exchanges on different active site ensembles and their resulting exchange energy for the β_1 phase.

Almost all surface exchanges performed have resulted in a positive energy, therefore surface reorganization and breaking of the active site is unlikely. For the $Pd_{10}Zn_{6}$ _1 101 facet exchange (Table 3.7b), the energy was slightly negative. However, when looking at the atom exchange performed, the active site is not broken, but is simply moved up. Therefore, the geometric effects of the active site are not broken, and an electronic effect related to the surface and subsurface atoms may allow for small shifts of the active site on the surface. The $Pd_{10}Zn_{6}$ _1 001 facet exchange (Table 3.7e) exhibited an obviously favorable result for the exchange. This exchange made the surface more like that of the more-studied Pd_1Zn_1 surface that contains "offset" monomers.

3.3.4. Surface stability through subsurface exchange calculations

Subsurface exchange energies were calculated to further evaluate the stability of the obtained β_1 phase active sites. As shown in in Figure 3.3, each bulk structure has a differing inner atom arrangement. Besides the central Pd atom, all other Pd atoms exist through a substitution in the β_1 phase unit cell of Pd into an once Zn site. During subsurface exchange calculations, Pd in these Zn subsurface sites were exchanged with Zn on the surface. The likeliness of this exchange was evaluated through the change in energy ($\Delta E = E_{exchanged} - E_{Original}$), where a positive value would indicate that the non-exchanged surface is more stable. Table 3.8 shows subsurface exchanges and their energies for four of the five possible surface ensembles (Table 3.1). One of the surface (Pd₁₀Zn₆_1 001, "in-line monomers" ensemble) could only be utilized for these calculations if the surface utilized was double in thickness of all other surfaces, thus it was not included in this set of calculations.

Facet and Ensemble	Before Exchange	After Exchange	ΔE (eV)
(a) Pd10Zn6_1 101 "X"			-0.23 eV
(b) Pd10Zn6_1 101 "X"			-0.05 eV
(c) Pd10Zn6_1 011 "Triple"			0.07 eV
(d) Pd10Zn6_2 101 "Off-set monomers"			-0.09 eV
(e) Pd10Zn6_3 001 "Boxed"			-0.31 eV

Table 3.8. Subsurface exchanges on different active site ensembles and the resulting exchange
energies for the β_1 phase

Almost all subsurface exchanges resulted in significant negative exchange energy. This suggests that subsurface Pd that was substitutionally added to the β_1 unit cell prefers to orient itself on the surface, breaking the unique active sites of each facet. This leads to the high possibility that any Pd added into the unit cell will preferentially go to the surface, which leads to the potential of a surface that is fully Pd. The resulting catalyst would be a Pd shell with some sort of Pd-Zn ensemble below the surface. Therefore, the β_1 phase cannot be utilized as a catalyst with unique active site ensembles by substitution of additional Pd atoms.

3.4. Conclusions

While PdZn (1:1) may be a reliable intermetallic for obtaining Pd monomers isolated by Zn atoms, the inclusion of one or two extra Pd within the unit cell will result in a surface that would be mainly composed of Pd. Utilizing the normalized surface energies, stoichiometric and non-stoichiometric surface energies can be compared. Based on the resulting surface energies, it cannot definitively be known which surface had the lowest energy or most stable. While all stoichiometric surfaces (Pd₁₀Zn₆1 101 and Pd₁₀Zn₆2 011 facets) resulted in the "X" active site ensemble, two non-stoichiometric surfaces resulted in all possible surface energies being lower than that of the lowest stoichiometric surfaces, $Pd_{10}Zn_6 = 1011$ and $Pd_{10}Zn_6 = 3011$ facets, which have the "triple" and "X" ensembles, respectively. When further surface exchange calculations were performed, it was noted that the resulting active site ensembles are seen to stably exist (except the Pd₁₀Zn₆_1 001 surface). However, based on surface stability calculations through exchanging Pd from subsurface locations to the surface, it was shown that including more Pd to the surface is generally more favorable than maintaining the unique active site ensembles that were originally found. Thus, it is inferenced that the resulting catalyst would be a Pd shell with a varying Pd-Zn subsurface, therefore no unique active sites can be found within the beta phase of Pd-Zn.

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CHAPTER 4 Summary of thesis and future work

4.1. Thesis summary

The vast application of intermetallics has been fully recognized and is continuing to grow. Strides have been made by numerous researchers to address the need for a better understanding of the process and to further explore other possibilities for continuous advancement. Knowing fully well that an understanding of active site requirements is a critical aspect has motivated the research group to undertake this current study that is focused on (1) investigating and understanding the particular γ -brass active site for other alkenes, (2) adapting the existing γ -brass active site through the use of a ternary Pd-M-Zn catalyst, and (3) exploring other phases to better understand the different active sites for potential use for acetylene semi-hydrogenation and other chemistries. In this thesis, the use of the γ -brass and β_1 Pd-Zn phases have been investigated to better understand active site requirements and to find possible new active sites, respectively.

The possibility of utilizing propylene in place of ethylene for expensive isotopically labeled hydrogenation experiments on Pd-Zn γ -brass were examined using DFT. Ethylene and propylene were observed to adsorb similarly to the γ -brass surface when van der Waals forces were considered. Calculated activation energies indicated that the initial diffusion of hydrogen over a Pd₃ trimer towards the adsorbate had two possible pathways, where it is hypothesized that the identity of the adsorbate should not affect the activation energy. The first hydrogenation step of the adsorbate showed similar activation energies for ethylene and propylene_C1 (hydrogenating the carbon with the additional methyl group). The activation energy of the hydrogenation of propylene_C2 was seen to be larger than that of ethylene and propylene_C1, suggesting it is less

likely to occur. These results suggest that propylene has the possibility of being used as a surrogate in hydrogenation reactions that would require ethylene

Ternary Pd-M-Zn γ-brass catalysts were synthesized through solid state diffusion. The catalyst identity was confirmed through XRD, Rietveld refinement, and ICP-OES. The XRD confirmed that the synthesized catalyst contained the γ-brass phase. Rietveld refinement of the diffractogram confirmed atom locations/site occupancies of each element in the unit cell. This confirmed that the ternary metal will appear in the central atom of the trimer site. The ICP-OES was performed to obtain the composition of each catalyst; it was confirmed that the synthesized catalysts were near that of the intended compositions: Pd₉Zn₄₃, Pd₉CuZn₄₃, Pd₉AuZn₄₃, Pd₉AuZn₄₃, Pd₉AgZn₄₃. Ternary Pd-M-Zn γ-brass catalysts could offer further selectivity control in hydrogenation through introduction of the additional M atom in Pd-M-Pd trimer active sites.

The upper Pd limits of the β_1 phase (Pd₉Zn₇ and Pd₁₀Zn₆) were studied utilizing DFT to understand possible bulk and surface constructions and their relation to each other in terms of stability. Five possible active site ensembles were identified from low index facets. These low index facets resulted in surfaces that were both stoichiometric (number of atoms are multiple of that of the bulk composition) and non-stoichiometric surfaces. All stoichiometric surfaces resulted in facets with the "X" ensemble while non-stoichiometric surfaces had the possibility of being any of the five possible facets. A single surface could not be definitively selected as most energetically favorable to exist. The lowest energy surfaces were two non-stoichiometric surfaces with different active site ensembles (X and triple) with overlapping surface energies. Further testing of the stability of the active site ensembles were performed through surface and subsurface exchanges. Surface exchange energies revealed that all facets preferred to exist as the initially found active site. Subsurface exchanges, on the other hand, showed that many surfaces would preferentially have the Pd that was added to the Pd_1Zn_1 unit cell to appear on the surface. Therefore, it was deemed that this surface would more likely result in a Pd surface with Pd-Zn subsurface arrangements, thus, no unique active sites may exist.

4.2. Future work

4.2.1. Ethylene hydrogenation kinetic studies on ternary Pd-M-Zn γ-brass catalysts

Olefin (specifically ethylene) hydrogenation is a commonly studied model probe reaction with its simplistic reaction path and its utility to industry¹⁻⁴. Due to its industrial importance, understanding its mechanism to allow for optimization is highly desired. Ethylene hydrogenation mechanisms have been studied through the basis of the Horiuti-Polyani mechanism⁵⁻⁷. This mechanism occurs through adsorption of the alkene to the surface, followed by sequential hydrogenation of the alkene.

Previous research in our group has been able to work towards understanding the γ -brass active site through the utilization of experiments and DFT⁸. Current studies that utilize experiments, DFT, and MKM to understand ethylene hydrogenation mechanism on the Pd₉Zn₄₃ catalyst are ongoing within our group (by He and Dasgupta).

To understand ethylene hydrogenation on the ternary Pd-M-Zn γ -brass surface, similar experiments are proposed. While preliminary experiments have helped in understanding the various trimers activity and selectivity in co-fed acetylene and ethylene hydrogenation experiments⁸, full hydrogenation kinetic studies have not been performed for either reactant. Therefore, utilizing a flow reactor with strictly differential conversion, ethylene hydrogenation experiments at various temperatures and ethylene and hydrogen partial pressures should be performed to obtain the activation energy and reaction orders. Performing these experiments in collaboration with DFT and microkinetic modeling will be a powerful tool in understanding the specific hydrogenation mechanism of ethylene on the various trimer surfaces.

4.2.2. Congruent melting of Pd and Zn for γ -brass catalyst synthesis

Through current synthesis methods, the bulk γ -brass phase catalyst, much like many other bulk intermetallic catalysts are formed by simply adding metals into a crucible and annealing them under vacuum⁹⁻¹². Additionally, the γ -brass phase has been synthesized as nanoparticles through dry impregnation and strong electrostatic adsorption¹³.

When observing the Pd-Zn phase diagram (Figure 2.1) a congruent melting point can be seen in the γ -brass phase at 1153 K for ~Pd₁₀Zn₄₂. At this temperature, the composition of both the liquid and solid phases are identical and slowly cooling the metals to a solid may lead to the formation of large crystal sized catalysts. These large crystal sizes can result in higher resolution related to characterization, such as the use of X-ray diffraction (XRD) and scanning electron microscopy (SEM)¹⁴.

Much like the synthesis method utilizing solid state diffusion (Section 2.3.1.1.), Pd and Zn powders will be added to a crucible, plugged with quartz wool, and vacuum sealed in a quartz ampoule. However, synthesis in the box furnace will occur at a higher temperature, heating the metals up to the congruent melting point, 1153 K, then slowly cooling the liquid to a solid. A resulting ingot will be obtained and later milled to a powder. However, it is noted that Zn evaporation will occur due to the high temperature and low pressure (1179 K at 1 atm). This may result in Zn escaping the crucible and when cooling, would stick to the walls of the ampoule. While utilizing a different set-up for synthesis may be possible, the evaporation of Zn while Pd is a liquid

may lead to only a small extent of Pd and Zn mixing, therefore synthesis testing with different amounts of Zn may lead to the most optimal method of utilizing this synthesis method.

4.2.3. Competitive hydrogenation of benzene and ethylene

A previous study performed in our group⁷ observed the competitive hydrogenation linear alkenes and aromatics on various catalysts, computationally and experimentally. This reaction is important in the pyrosis gas (pygas) upgrading/hydrogenation process utilized to obtain important aromatics of benzene, toluene, and xylene (BTX). From the naphtha cracking process, typically used to obtain ethylene and propylene, pygas is produced, which contains a wide variety of compounds, which include olefins, diolefins, styrene, and BTX¹⁵. The olefins, diolefins and styrene all have the possibility of resulting in the formation of gum, which are large compounds with high molecular masses and are non-volatile. Therefore, a selective hydrogenation of the gumforming agents is desired to prevent gum formation and to maintain the desired BTX products.

Using DFT, this reaction was simplified and modeled utilizing ethylene as the olefin and benzene as the aromatic for hydrogenation. Adsorption of benzene and ethylene were studied on various hypothetical surfaces: pure metal surfaces, surfaces with a Pd monolayer on various metals, and Pd or Pt surfaces doped with Zn or Sn. These studies showed that on pure metal and Pd monolayer surfaces, both benzene and ethylene could bind to the surface. However, on the Pd/Pt doped surfaces, benzene would not adsorb to the surface, while ethylene would. This indicates the doped surface does not have the proper active site for benzene adsorption. Reaction experiments were performed by co-feeding ethylene and benzene into a reactor over Pd foil. It was observed that with increasing amounts of benzene in the feed, there was a decrease in ethylene hydrogenation. This suggests that benzene would preferentially bind to the Pd surface, which blocks active sites to allow for ethylene hydrogenation. These conclusions indicate that on pure metal surfaces, benzene and ethylene compete for active sites. However, ethylene hydrogenation may be able to occur in the presence of benzene when the surface is not a pure metal.

This previous study used hypothetical surfaces for DFT experiments and pure Pd for reaction experiments. It is observed that the hypothetical doped surfaces that were shown to exhibit different binding of benzene to the surface can be represented with DFT and reaction experiments with Pd-Zn intermetallic catalysts. The previously studied γ -brass and β_1 phases of Pd-Zn will be utilized for this study. Computational studies similar to the ethylene and propylene adsorption and hydrogenation study presented in Chapter 2 will be performed. Adsorption and hydrogenation studies be performed to understand the competitive hydrogenation preferences of benzene or ethylene to the γ -brass surfaces (Pd₈Zn₄₄ and Pd₉Zn₄₃) and the β_1 (Pd₁Zn₁) surface. Adsorption energies of both benzene and ethylene will be compared followed by a comparison of hydrogenation activation energies. This will help provide a better understanding of the preference of each surface for competitive hydrogenation.

Reaction experiments will begin with the synthesis of each catalyst (Pd₈Zn₄₄, Pd₉Zn₄₃, and Pd₁Zn₁) through methods similar to that in Section 2.3.1. Following characterization of each catalyst through ICP-OES and XRD, reactivity experiments will be performed. Kinetic studies (obtaining experimental activation energies and reaction orders) will be performed utilizing a flow reaction with strictly differential conversion. Benzene and ethylene will be co-fed into a reactor and the products will be observed on-line with a gas chromatograph.

Results of both computational and reaction experiments will help us better understand the actuality of the study previously performed (by our group) on the proposed possibility of selective hydrogenation of an alkene on a surface similar to that of an intermetallic surface.

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