The Pennsylvania State University
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NICKEL-ZINC INTERMETALLIC CATALYSTS FOR ACETYLENE SEMI-
HYDROGENATION AND X-RAY ABSORPTION SPECTROSCOPY TECHNIQUES
FOR CATALYST CHARACTERIZATION

A Dissertation in
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by
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ABSTRACT

The development of new catalytic materials to improve the activity and selectivity of catalytic reactions is an ongoing task for researchers due to the continual demand for cheaper, more energy efficient methods to produce both new and existing products. This dissertation focuses on developing base-metal catalysts for selective hydrogenation reactions. In particular, Ni-Zn intermetallic compounds (which are ordered arrangements of these two elements) are utilized for the selective semi-hydrogenation of acetylene, which is a high-volume industrial reaction that currently requires the use of precious metal catalysts. The poor catalytic properties of pure Ni are greatly improved through the addition of a second base metal, Zn, making the Ni-based catalysts behave more like precious metals. While we cannot perform alchemy, turning two base metals into an intermetallic material that behaves like a precious metal might be the closest we can come. The synthesis of well-defined materials and corresponding kinetic measurements utilizing isotopic labeling are combined with density functional theory calculations to highlight the reasons for the enhanced selectivity of Ni-Zn intermetallic catalysts. In situ structure-determination during catalyst synthesis helps to lay the framework for future intermetallic catalyst development.

Developing new catalytic materials requires detailed knowledge of catalyst structure, because structure is related to function. New characterization methods that have the ability to provide better descriptions of catalysts have the potential to be used in many sub-fields of catalysis. To address this need, this dissertation also focuses on new catalyst characterization techniques using X-ray absorption spectroscopy. We use differential X-ray absorption fine structure to monitor the Ar-induced surface restructuring of Pd nanoclusters at 77 K, highlighting the ability of this technique to probe surface atoms of Pd nanoclusters. Furthermore, we use X-ray absorption near edge structure to identify second-shell coordination in Ti-based transition metal complexes.
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Chapter 1

Introduction

1.1. Acetylene Semi-Hydrogenation

Materials that can selectively catalyze reactions such that they follow a desired reaction path are far reaching. Perhaps one of the most important industrial reactions for which selectivity is a must is the selective semi-hydrogenation of acetylene in excess ethylene. Acetylene is present as an impurity in ethylene feed streams for ethylene polymerization. At a level of 0.5 – 2.0 %, acetylene must be reduced to less than 5 ppm prior to polymerization to prevent poisoning of the ethylene polymerization catalyst.¹² A highly selective catalyst for this reaction converts all of the acetylene to ethylene, thereby boosting the amount of the ethylene feedstock. The undesired pathways for this reaction include both the over-hydrogenation of ethylene to form ethane and the oligomerization of acetylene to form higher molecular weight compounds. Over-hydrogenation leads to a loss in the ethylene feedstock and the risk of excessive heat production and reactor runaway. Oligomerization results in the formation of high molecular weight compounds (often termed “green oil”) that plug the reactor and lead to eventual catalyst deactivation. The desired reaction pathway is summarized in Figure 1-1.
Figure 1-1. Desired reaction scheme for acetylene semi-hydrogenation. Undesired reaction pathways are denoted with red Xs.
Pd-based catalysts are the industrial catalyst of choice for acetylene semi-hydrogenation. While monometallic Pd/Al₂O₃ and Pd/SiO₂ are widely used for the upgrading of olefins, the selectivities of these catalysts are not sufficient to warrant their use in acetylene semi-hydrogenation due to their propensity for both over-hydrogenation and oligomerization.³⁴ The addition of Ag to form Pd-Ag alloy catalysts results in more selective catalysts with little tendency for over-hydrogenation due to a lower surface coverage of hydrogen under reaction conditions.⁴⁻¹² Pd-Ag catalysts have remained the most widely used industrial catalysts for acetylene semi-hydrogenation in excess ethylene since they were first patented in 1957.¹³ More recently, Pd-Ga intermetallic compounds have been shown to exhibit high ethylene selectivity and long-term stability due to the isolation of Pd active sites in a well-defined intermetallic structure.¹⁴⁻¹⁸ There has been recent interest in replacing Pd-based catalysts with base metals, as platinum-group metals are a limited resource with high monetary and environmental costs of production compared to base metals.

1.2. Base-Metal Hydrogenation Catalysts

Replacement of Pd-based hydrogenation catalysts with elements from the 3d transition metals such as Fe, Ni, and Cu poses unique challenges that can be overcome through the addition of a second element. For example, Fe catalysts require high temperature and pressure for the hydrogenation of acetylene and ethylene. The addition of Al to Fe to form intermetallic Al₁₃Fe₄ greatly improves the selectivity as a result of the alteration of the electronic structure of Fe and active site isolation.¹⁹ Cu-based catalysts that have a high tendency to form oligomers have been made more selective through the addition of Ni, which increases the ability of the catalyst to dissociate hydrogen.²⁰⁻²² In this work, we focus on Ni-based catalysts, which tend towards both over-hydrogenation and oligomerization when used as acetylene semi-hydrogenation catalysts.²³
Specifically, we focus on intermetallic Ni-Zn compounds which were previously suggested to exhibit good selectivity for acetylene semi-hydrogenation in the presence of excess ethylene.  

1.3. Intermetallic Compounds

An intermetallic compound is a material that contains two or more metals in an ordered arrangement. This is contrasted with an alloy, which contains a disordered, or random, arrangement of elements. This concept is illustrated in Figure 1-2. Since intermetallic compounds crystallize in an ordered crystallographic structure, they contain homogenous active sites, compared to a heterogeneous distribution of sites in an alloy. Thus, intermetallic compounds lend themselves to selective reactions where one particular pathway is preferred over another. Furthermore, the bonding in intermetallic compounds is partly ionic or covalent which typically leads to higher stability and less segregation compared to alloys. This is particularly important for base-metal intermetallic compounds which are highly oxophillic in nature. Most importantly, intermetallic compounds allow for active-site isolation, where an active metal can be diluted in the matrix of another inactive metal to potentially produce a selective catalyst.
Figure 1-2. Contrast between alloy with a random arrangement of elements (left) and intermetallic with an ordered arrangement of elements (right).
1.4. X-ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) is widely used in catalysis due to its ability to probe the atomic structure of catalysts. Figure 1-3A shows a typical setup for an X-ray absorption spectroscopy experiment, where the absorption coefficient, $\mu(E)$, is measured by taking the log of the ratio of the intensities of the inlet X-ray beam, $I_0$, and the transmitted X-ray beam, $I_t$. The parts of a typical XAS X-ray absorption coefficient-versus-energy plot include the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions (Figure 1-3B). XANES contains information regarding the oxidation state (and coordination geometry in some cases) of the material being tested, while EXAFS is most useful for determining bond lengths, identities, and geometry of neighboring atoms.$^{28-33}$ Some of the limitations of XANES and EXAFS that we aim to improve upon are discussed below.
Figure 1-3. (a) Transmission geometry of a typical XAS experiment showing how the absorption coefficient, $\mu(E)$ is measured. (b) Illustration of the absorption coefficient as a function of energy during a typical X-ray absorption spectroscopy experiment. The X-ray absorption near edge structure (XANES) and extended X-ray absorption near edge structure (EXAFS) regions are indicated in the plot.
EXAFS measures local structure, but is inherently insensitive to the surface structure of materials. In catalysis, it is the surface atoms that control the catalytic properties of the materials.\(^\text{34-38}\) Thus, detecting the number and coordination environment of the surface metal atoms of catalysts (in particular: bimetallic catalysts) is of utmost importance in understanding catalytic behavior. To make EXAFS a surface sensitive technique, external stimulation such as the chemisorption of molecules is required to enhance the detectability by EXAFS.\(^\text{39}\) The use of differential EXAFS has been shown to allow for more sensitive detection of local structure compared to traditional EXAFS.\(^\text{40-45}\) We will show the application of a differential X-ray absorption spectroscopy (Δ-EXAFS) technique that we developed to detect surface atoms of supported Pd nanoclusters using Ar as an atomic probe.

XANES is very useful for catalytic systems due to its ability to be used in situ.\(^\text{46}\) Compared to EXAFS, it can be performed very quickly and on low weight loading samples. However, the information that can be determined with XANES is limited to oxidation state and the first coordination shell geometry. Furthermore, the interpretation of XANES generally requires complete structural information or experimental XANES spectra of model compounds for comparison.\(^\text{47-48}\) An additional drawback of XANES is that it is only useful for determining first shell coordination, while there are many examples in the literature where the elements in the second shell coordination sphere of catalysts can dramatically change their activity.\(^\text{31, 33, 49-50}\) We will show how density functional theory (DFT) structural optimization and ab initio XANES calculations can be used to help identify second shell atoms in molecular titanium species with demonstrated catalytic activity.
1.5. Summary of the Dissertation

Chapters 2, 3, and 4 are studies regarding intermetallic Ni-Zn catalysts for the selective semi-hydrogenation of acetylene. Chapters 5 and 6 focus on the development of new techniques using X-ray absorption spectroscopy to characterize the active sites of catalysts. More specifically, Chapter 2 contains a study of the selectivity of bulk intermetallic Ni-Zn catalysts for acetylene semi-hydrogenation in excess ethylene. Bulk catalysts with well-defined crystal structures were chosen for this study to eliminate the effects of the catalyst support and a heterogeneous mixture of active site on selectivity, thus enabling us to learn the fundamental reasons for the enhanced selectivity of Ni-Zn catalysts for acetylene semi-hydrogenation. The results of detailed selectivity studies using isotopic labeling were combined with density functional theory (DFT) calculations to provide additional insights into the mechanism for the increased selectivity of Ni-Zn catalysts. In order to create an industrially-useful intermetallic Ni-Zn catalyst, a high surface area, supported, catalyst is required. Therefore, Chapter 3 provides a study aimed at creating supported nanoparticle intermetallic Ni-Zn catalysts from divalent Ni and Zn precursors. XAS was used to investigate the phase transformation of Ni nanoparticles (NPs) to intermetallic β1-NiZn NPs during the in situ reduction of Ni1-xZnx/ZnO catalysts and to show the mechanism by which intermetallic β1-NiZn is formed. This study elucidates the difficulties that arise when extrapolating from DFT or bulk materials to supported catalysts. Chapter 4 provides a detailed investigation into a specific crystal structure in the Ni-Zn phase diagram: the γ-Brass crystal structure. This structure is unique as it has both the ability to create Ni atoms that are perfectly isolated by Zn atoms as well as the ability to create clusters of Ni atoms, dependent on Ni concentration. Catalytic H2-D2 exchange experiments were used to help better understand the surface concentration of Ni and Zn sites in this material. Furthermore, Chapter 4 discusses the relevance of γ-Brass crystal in isolating other catalytically-active elements including Pd and Pt.
Chapter 5 addresses the need for characterization methods that are sensitive to the surface elements in multi-component catalysts. The need for such methods was realized when we asked the following question about our Ni-Zn catalysts: What do the surfaces (i.e. atomic layers of atoms) of the Ni-Zn particles actually look like? Chapter 5 provides a model study using supported Pd nanoclusters, where Ar was adsorbed at 77 K and XAS was used to probe the under-coordinated surface atoms of the Pd nanoclusters. A combination of experiment and theory were used to show that XAS could be used to probe ultra-small changes in the surface atoms of the Pd catalyst. Finally, Chapter 6 shows how XANES can be used to identify the atoms in the second coordination shell of Ti-based transition metal complexes. The calculation of theoretical XANES spectra from DFT-optimized structure geometries helps to show the usefulness of this method and provides an explanation for signatures in the XANES spectra that are indicative of second-shell coordination.
1.6. References


Chapter 2

Zinc Inclusion to Heterogeneous Nickel Catalysts Reduces Oligomerization during the Semi-hydrogenation of Acetylene


2.1. Introduction

The catalytic semi-hydrogenation of acetylene to produce ethylene is a common method for the removal of trace acetylene (0.5 - 2% by volume) in ethylene feed streams destined for ethylene polymerization \(^1\). Acetylene impurities in ethylene produced from naphtha, responsible for the deactivation of the polymerization catalyst, must be reduced to a level of 5 ppm prior to polymerization \(^2\). A good catalyst for this reaction converts all of the acetylene to ethylene without further converting any ethylene to ethane such that there is a net increase in the amount of ethylene. Well-dispersed palladium supported on metal oxides exhibits high activity for acetylene removal, but limited selectivity as a result of over-hydrogenation to ethane and limited long-term stability as a result of oligomer ("green oil") accumulation \(^3\)-\(^4\). The addition of silver to palladium catalysts results in a higher ethylene selectivity due to a decrease in hydrogen coverage and a reduction in the hydrogenation of gas-phase ethylene \(^4\)-\(^12\). More recently, intermetallic Pd-Ga compounds demonstrated high ethylene selectivity and long-term stability due to isolation of the Pd active sites in a well-defined intermetallic structure \(^13\)-\(^17\). Isolated Pd atoms reduce the ability of the catalyst to over-hydrogenate ethylene to form ethane, produce oligomerization products, and form coke on the catalyst surface. However, there exists room for catalyst improvement, particularly in terms of cost.

Intermetallic NiZn was identified as a low-cost replacement for Pd-Ag catalysts by Studt et al. using a density functional theory (DFT) scaling analysis across alloys of late 3D transition
metals. Nickel-zinc catalysts were subsequently synthesized by co-impregnation of nickel and zinc nitrates on a MgAl₂O₄ support, reduced at 400 °C, and tested for the catalytic hydrogenation of acetylene in the presence of ethylene. Structural characterization, however, was not included in the study of Studt et al. to prove the existence of intermetallic NiZn. Furthermore, it has since been shown that nickel-zinc catalysts synthesized by the method of Studt et al. do not contain intermetallic NiZn. A temperature of 400 °C is not sufficient for the reduction of ZnO (which is present after calcination of zinc nitrate) such that the catalyst contains a mixture of Ni and ZnO phases after reduction. An additional shortcoming in previous studies of nickel-zinc catalysts is the measure of ethylene selectivity. Studt et al. used ethane concentration as a descriptor for ethylene selectivity where a low ethane concentration was related to a high ethylene selectivity. However, it is well known that acetylene oligomerizes on Ni-based hydrogenation catalysts and that ethane is only one of many products of the reaction. In addition, acetylene may dissociatively adsorb to ZnO, depositing carbon atoms on the surface. Thus, it is important to measure ethylene formation directly rather than inferring the concentration based on ethane formation.

Scheme 1 summarizes the possible pathways for the reaction of a mixture of acetylene, ethylene, and hydrogen on Ni-based catalysts. According to Scheme 1, acetylene and ethylene competitively adsorb to the catalyst surface, where adsorbed species are denoted with an asterisk (*). Acetylene that has been partially hydrogenated may either react with another adsorbed hydrogen to form adsorbed ethylene or react with an adsorbed acetylene to form oligomers (leading eventually to "green oil"), the simplest of which is butadiene (C₄H₆). Previous work has suggested that C₂H₃* and adsorbed acetylene are the precursors for oligomer formation. Finally, adsorbed ethylene may either desorb to form gas-phase ethylene (desired product), or further hydrogenate to form ethane. During catalysis, ethane produced from ethylene is indistinguishable from ethane produced from acetylene. In addition, it is impossible to quantify
the ethylene that is produced from $^{12}$C acetylene when the reaction is run with excess $^{12}$C ethylene.
Scheme 2-1. Proposed reaction routes during the hydrogenation of acetylene in the presence of ethylene.

\[
\begin{align*}
\text{C}_2\text{H}_2(\text{g}) & \rightarrow \text{C}_2\text{H}_2^* \rightarrow \text{C}_2\text{H}_3^* \rightarrow \text{C}_2\text{H}_4^* \rightarrow \text{C}_2\text{H}_4(\text{g}) \quad \text{desired} \\
\text{C}_2\text{H}_6(\text{g}) & \rightarrow \text{C}_2\text{H}_6(\text{g}) \quad \text{undesired} \\
\text{C}_2\text{H}_4(\text{g}) & \rightarrow \text{C}_2\text{H}_4^* \rightarrow \text{C}_2\text{H}_8(\text{g}) \quad \text{undesired} \\
& \quad \text{green oil} \quad \text{undesired}
\end{align*}
\]

*Adsorbed species are denoted with an asterisk (*) and solid arrows denote elementary steps.
Herein, we employ a bulk synthesis method to create intermetallic nickel-zinc compounds with well-defined structures. We use isotopic labeling of the carbon atoms in acetylene, where the reactant mixture consists of $^{13}$C$_2$H$_2$, $^{12}$C$_2$H$_4$, and H$_2$. Isotopic labeling has been used previously to elucidate the mechanism for acetylene hydrogenation on Pd and Pt catalysts\textsuperscript{31-34}. To the best of our knowledge, there are no previous reports of isotopic labeling for acetylene hydrogenation on Ni catalysts. We use isotopic labeling in a batch reactor to evaluate each of the pathways proposed in Scheme 1 and provide an overall measure of ethylene selectivity. Ethylene selectivity is defined as the net ethylene production per acetylene removal (eq 1).

\[
\text{Ethylene Selectivity} = \frac{P_{^{13}\text{C}_2\text{H}_4,t} - P_{^{12}\text{C}_2\text{H}_6,t}}{P_{^{13}\text{C}_2\text{H}_4,i} - P_{^{13}\text{C}_2\text{H}_2,t}} \tag{1}
\]

The ethylene produced from acetylene is directly measured as the amount of $^{13}$C$_2$H$_4$. The gas-phase ethylene that reacts to form ethane is measured as the amount of $^{12}$C$_2$H$_6$. Then, the net ethylene production is defined as the amount of $^{13}$C$_2$H$_4$ formed minus the amount of $^{12}$C$_2$H$_6$ formed. Acetylene removal is quantified by taking the difference between the initial and final amounts of acetylene in the reactor. Eq 1 gives the expression for ethylene selectivity, where $P_X$ is the partial pressure of component X, i is the initial time, and t is the time at which the selectivity is being measured. By this definition, the maximum in ethylene selectivity is 1 and ethylene selectivity may be negative, which corresponds to a net decrease in the amount of ethylene. Acetylene conversion is defined as the decrease in partial pressure of acetylene at time, t, divided by the initial partial pressure of acetylene (eq 2). Selectivity for all other products of the reaction is defined in eq 3, where $N_x$ is the number of carbon atoms in component X. The term $N_x/2$ normalizes the data with respect to the number of carbon atoms in acetylene.
We use density functional theory (DFT) methods to generate the reaction energy diagram for hydrogenation and oligomerization pathways on pure Ni and intermetallic NiZn. A comparison is made between the selectivities of Ni and intermetallic NiZn using Langmuir-Hinshelwood kinetics. The reaction energy diagram for acetylene hydrogenation on intermetallic NiZn has been previously calculated, but neither a microkinetic analysis nor a comparison with pure Ni was made. In this manuscript, we apply experimental and theoretical methods for determining the effect of Zn content on the selectivity of Ni catalysts for the semi-hydrogenation of acetylene.
2.2. Experimental Methods

2.2.1. Synthesis of Bulk Intermetallic Compounds

Bulk intermetallic Ni-Zn compounds were synthesized by solid-state diffusion in quartz tubes evacuated to a pressure of ~30 mTorr. Ni powder (Sigma Aldrich, <150 μm particle size, 99.999%) and Zn granules (Sigma Aldrich, 3 mm diam, 99.99%) were added with the correct stoichiometry to an alumina crucible (LSP Ceramics, 13 mm i.d.) and sealed in an evacuated quartz tube. NiZn and Ni$_5$Zn$_{21}$ were heated to 700 °C at a ramp rate of 10 °C/min, held for 24 h, and cooled to RT at a ramp rate of 1 °C/min. Ni$_4$Zn was heated to 900 °C at a ramp rate of 10 °C/min, held for 24 h, and cooled to RT at a ramp rate of 3 °C/min. Pure Ni was also subjected to an identical treatment to Ni$_2$Zn. The samples were removed from the quartz tubes and loaded into a stainless steel ball mill (SPEX Mixer/Mill, 8001 sample container) along with 1 mL of 1,1,1,2,2,3,4,5,5,5-decafluoropentane (Vertrel XF, Dupont) per gram of sample within an argon-filled glove box (< 1 ppm oxygen). The samples were removed from the glove box in the sealed milling container and milled for 4 h in an argon atmosphere. After milling, the samples were placed in the glove box and the decafluoropentane was allowed to evaporate at room temperature. Samples were stored in the glove box prior to catalytic measurements.

2.2.2. Catalyst Characterization

Powder X-ray diffraction (XRD) data were collected on a PANalytical Empyrean X-ray diffractometer using Cu K$_\alpha$ ($\lambda$=1.5418 Å) radiation. Samples were prepared for analysis by filling the cavity of a silicon zero background holder and leveling the surface with a glass slide. The Empyrean has a diffractometer radius of 240 mm and is equipped with a PIXcel detector using scanning line mode (1D) detection. The incident beam optics had the following configuration: $\frac{1}{2}^\circ$
antiscatter slit, 10 mm beam mask, \( \frac{1}{4}^\circ \) fixed divergence slit, and 0.04 rad soller slits. The diffracted beam optics had the following configuration: 0.04 rad soller slits, Ni beta-filter, and \( \frac{1}{4}^\circ \) antiscatter slit. Data were acquired with a 0.025\(^{\circ}\) 2\(\Theta\) step size from 20 – 90\(^{\circ}\) 2\(\Theta\). Rietveld refinement was performed within Jade (version 2.2.0 (2010) Materials Data Incorporated) to determine the unit cell parameters from the X-ray diffraction data. A 5\(^{th}\) order polynomial background function and the default peak shape parameters were used within Jade for the Rietveld refinement. Visualization of the unit cells was performed with Materials Studio.

Nitrogen BET surface area measurements were performed using a Micromeritics Gemini V Surface Area Analyzer. 1 to 2 grams of sample was used for each measurement. Scanning electron microscopy (SEM) was performed with an FEI Nova NanoSEM 630. Catalysts powders were dispersed in ethanol and dropped onto silicon wafers. Images were taken at 1,000x magnification using an Everhart-Thornley detector (ETD) and an accelerating voltage of 5 kV.

2.2.3. Catalysis

Catalysis experiments were performed in a batch reactor. In a glove box, catalysts were loaded into a 1/2" OD quartz tube and supported with a plug of quartz wool on both sides of the catalyst bed. The quartz reactor tube was fit to the batch reactor with Swagelok Ultra Torr fittings. The reactor is a closed-loop system with a total volume of 33 mL and a three-way valve for admission of reactant gases. After loading catalyst, the system was evacuated to a pressure \(~120\) mTorr (monitored with Varian 531 gauge tube). Prior to admission of reactant gases, the Varian 531 tube was isolated from the system with a ball valve. The Varian 531 thermocouple gauge operates with a Pd-Au filament that will catalyze acetylene and ethylene hydrogenation if not isolated from the system prior to addition of reactants. \(^{13}\)C\(_2\) acetylene (Sigma Aldrich) was added to the reactor through a needle valve to a pressure of \(~2.5\) Torr. The starting pressure of acetylene was 2.2, 3.1, 2.2, and 2.8 Torr for Ni, Ni\(_4\)Zn, NiZn, and Ni\(_5\)Zn\(_{21}\), respectively. The
acetylene pressure varied due to the experimental difficulty in accurately adding 2.5 Torr acetylene to the reactor. Subsequently, 10% hydrogen/helium was added to the reactor through a needle valve, to a total pressure of ~267 Torr. 10% ethylene/helium was then added to the reactor to reach a final pressure of ~800 Torr. The reactor was operated above ambient pressure to reduce contamination by air. Reactants were circulated at a flow rate of ~50-100 mL/min (> 50 bed volumes per minute) using a diaphragm circulation pump. Since the batch system contains no measure of this recirculation rate, the flow rate of circulation pump was measured ex situ and was slightly different for each experiment. The high circulation flow rate minimizes any external heat or mass transfer effects (a complete discussion of mass transfer effects may be found in the supplementary information at the end of this chapter). Samples were removed from the reactor for analysis with a 50 μL gas tight syringe (Hamilton). At least two samples were taken before heating the reactor to verify the initial concentration of acetylene. Heating from room temperature to the reaction temperature of 160 °C took approximately 10 min. The syringe was purged with sample gas twice prior to taking a sample for analysis. Sample analysis was performed on a Shimadzu GCMS-QP2010 Ultra gas chromatograph (GC) equipped with a mass spectrometer (MS). An alumina capillary column (Rt®-Alumina BOND/KCl, 30 m, 0.25 mm i.d.) was used to separate the gas mixture with a temperature program consisting of two minutes at 60 °C and a 10 °C/min ramp to 180 °C, with a total run time of 14 min. The column provides good separation of all of the C₂-C₄ hydrocarbons with the following elution order: ethane, ethylene, propane, propylene, acetylene, isobutane, butane, trans-2-butene, 1-butene, isobutylene, cis-2-butene, and 1,3-butadiene. Methane was presumably produced by the reaction, but due to the limitations of our experimental protocol, was not quantified. Air (present in the needle of the syringe used for injections) elutes from the column at the same time as methane in a broad peak and could not be deconvoluted due to the similarity in mass fragments of methane with oxygen and nitrogen. The MS was scanned from 12 to 100 m/z every 80 ms, where the sum of these ions is referred to as the total ion count (TIC). Quantification of the components was performed by integrating the TIC
and comparing the peak areas to a calibration standard (100 ppm each compound, SCOTTY gas calibration standard). The percentage of $^{13}$C$_2$ ethylene was determined by fitting the ionization spectra of the ethylene peak to a linear combination of the ionization spectra for natural ethylene and $^{13}$C$_2$ ethylene. An identical procedure was done for ethane. To account for differences in the injection volume, all peak areas were divided by the sum of the $^{12}$C$_2$H$_4$ and $^{12}$C$_2$H$_6$ peak areas since the sum of $^{12}$C$_2$H$_4$ and $^{12}$C$_2$H$_6$ remained constant throughout the experiment at a total pressure of 53 Torr. The starting pressure of $^{12}$C$_2$H$_4$ is 53 Torr and $^{12}$C$_2$H$_6$ is the only product of $^{12}$C$_2$H$_4$, thus the sum of $^{12}$C$_2$H$_4$ and $^{12}$C$_2$H$_6$ remain constant throughout the experiment.

2.2.4. Density Functional Theory (DFT) Methods

DFT calculations were carried out using the Vienna ab initio simulation program (VASP), an ab initio total energy and molecular dynamics program developed at the Institute for Material Physics at the University of Vienna 35-37. Ni and intermetallic NiZn were modeled as face-centered cubic (111) and L1$_0$ tetragonal (101) surfaces, respectively, with (4x4) surface unit cells and a slab thickness of 3 layers in the direction perpendicular to the surfaces. The lattice parameter for Ni was 3.52 Å. The lattice parameters for intermetallic NiZn were optimized to give the lowest energy structure and were a = 2.76 Å and c = 3.19 Å. Neighboring slabs were separated by 16 Å normal to the surface. Spin polarization was taken into account for all calculations with the exception of gas-phase optimization of molecules. The Perdew-Wang (PW91) version of the generalized gradient approximation (GGA) 38-39 was used with a plane wave basis set cutoff energy of 450 eV and a 3x3x1 Monkhorst-Pack k-point mesh 40. Structural optimization was carried out until the forces on all atoms were less than 0.05 eV/Å. The zero-point vibrational energy (ZPVE) was determined by calculating the harmonic vibrational modes for isolated molecules and adsorbed species. The climbing image-nudged elastic band (CL-NEB) method (implemented within the VASP code) was used for determination of transition states 41-43.
Four intermediate images were constructed between the initial and final states. Transition states were verified by ensuring they have a force tangent to the reaction coordinate of less than 0.05 eV/Å, a single imaginary vibrational frequency along the reaction coordinate, and atomic forces equivalent to our optimization criteria. The 0 K binding energies of adsorbates were calculated as the 0 K energy difference with ZVPE corrections between the adsorbed state and isolated molecule plus surface. Activation barriers were calculated as the 0 K energy difference between the transition and initial states. All activation energies are with respect to non-interacting adsorbed reactants.
2.3. Results

2.3.1. Structure of Intermetallic Ni-Zn Catalysts.

Three catalysts with compositions across the Ni-Zn phase diagram \(^{44-45}\) (Figure S2-1 of the supplementary information) were prepared to test the influence of Zn on the catalytic properties of Ni-based catalysts. Synthesis of the bulk compounds was performed in an air-free environment to yield phase-pure materials as evidenced by XRD (Figure 2-1).
Figure 2-1. X-ray diffraction patterns of Ni$_4$Zn, NiZn, and Ni$_5$Zn$_{21}$ catalysts. All of the observed peaks coincide with the calculated pattern of each structure. Insets show the atoms in the unit cell with Ni (light pink) and Zn (dark blue). Ni$_4$Zn forms a substitutional solid solution with the face centered cubic structure. NiZn forms the tetragonal L1$_0$ structure with each Ni atom coordinated by eight Zn nearest neighbors and 6 more distant Ni neighbors. Ni$_5$Zn$_{21}$ adopts the cubic γ-Brass structure with nickel atoms coordinated by 12 zinc atoms in an icosahedral geometry. Also shown is the stacking of the icosahedrons in the Ni$_5$Zn$_{21}$ structure.
Ni$_4$Zn is a substitutional solid solution with the face-centered cubic structure of nickel. Nickel and zinc atoms randomly occupy the sites of the structure with a lattice parameter (3.572 Å) that is slightly expanded compared to pure nickel (3.524 Å). On average, each Ni atom is coordinated by 9.6 Ni atoms and 2.4 Zn atoms. NiZn (JCPDS card 01-072-2668) forms a tetragonal unit cell (AuCu prototype) with space group $P4/mmm$ and cell parameters $a = 2.751$ Å, $c = 3.181$ Å. Ni atoms are coordinated by eight Zn atoms at a distance of 2.513 Å, four Ni atoms slightly farther away (2.751 Å), and two more distant Ni atoms (3.181 Å). Ni$_5$Zn$_{21}$ (JCPDS card 00-006-0653) forms the γ-brass structure which is cubic with space group $I4_3m$ (No. 217) with a lattice parameter of $a = 8.918$ Å. The Hume-Rothery principle of valence electrons predicts that the γ-brass structure has a valence electron concentration of 21 valence electrons per 13 atoms in the unit cell. Ni$_5$Zn$_{21}$ achieves this criterion of the Hume-Rothery principle with a total of 84 valence electrons in the unit cell composed of 52 atoms. Ni$_5$Zn$_{21}$ is composed of icosahedrons with a stacking pattern shown in the inset of Figure 2-1. Each icosahedron shares three faces and six corners with neighboring polyhedra. Neutron diffraction has been used to show that the Ni atoms occupy the outer tetrahedral icosahedral sites whereby each nickel atom is coordinated by 12 zinc atoms. The icosahedrons are termed “outer tetrahedral” because they share faces to form a tetrahedron at the center of the unit cell. The structure exhibits high similarity to that of the Cu-Zn system, where the smaller atoms (Ni or Cu) occupy the outer tetrahedral sites. The crystal structure data for the Ni-Zn compounds along with Rietveld refinements of the powder XRD data are summarized in Table 2-1. SEM images for each of the four catalysts are shown in Figure S2-2 of the supplementary information.
Table 2-1. Crystal structure data and results of Rietveld refinement for Ni-Zn catalysts.

<table>
<thead>
<tr>
<th>Material</th>
<th>Space Group</th>
<th>Pearson Symbol</th>
<th>Strukturbericht Designation</th>
<th>Prototype</th>
<th>Lattice Parameter(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Fm-3m</td>
<td>cF2</td>
<td>A1</td>
<td>Cu</td>
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</tr>
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<td>Fm-3m</td>
<td>cF2</td>
<td>A1</td>
<td>Cu</td>
<td>a = 3.572 Å</td>
</tr>
<tr>
<td>NiZn</td>
<td>P4/mmm</td>
<td>tP2</td>
<td>L1&lt;sub&gt;0&lt;/sub&gt;</td>
<td>AuCu</td>
<td>a = 2.751, c = 3.181 Å</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;5&lt;/sub&gt;Zn&lt;sub&gt;21&lt;/sub&gt;</td>
<td>43m</td>
<td>cI52(a)</td>
<td>D8&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Cu&lt;sub&gt;5&lt;/sub&gt;Zn&lt;sub&gt;8&lt;/sub&gt;</td>
<td>a = 8.918 Å</td>
</tr>
</tbody>
</table>

<sup>a</sup>Lattice parameters determined from Rietveld refinement of the powder XRD data.
2.3.2. Selectivity for the Semi-hydrogenation of Acetylene in Excess Ethylene

The time dependence of the catalytic hydrogenation of acetylene in the presence of ethylene is shown in Figure 2-2. The initial partial pressures for each of the reactions were ~2.5 Torr $^{13}$C$_2$H$_2$, 27 Torr H$_2$, and 53 Torr $^{12}$C$_2$H$_4$, which is approximately a 1:10:20 acetylene:hydrogen:ethylene ratio. Each reaction was carried out at 160 °C, while the time frame for acetylene removal was similar across each of the tests. This was accomplished by varying the amount of catalyst in the reactor; the most catalyst was required for Ni$_5$Zn$_{21}$, the sample with the lowest nickel content. By keeping the temperature constant, we are able to directly compare the selectivities of the Ni-Zn catalysts under identical conditions. The rate of acetylene disappearance on pure Ni (Figure 2-2A) has a 0.6 order dependence on acetylene concentration as the reaction proceeds. Ni$_4$Zn (Figure 2-2B) and NiZn (Figure 2-2C) show orders of 0.6 and 0.7, respectively. Ni$_5$Zn$_{21}$ (Figure 2-2D) shows a dependence of 1.0 on acetylene, which indicates a weaker binding of acetylene, presumably due to the high Zn content of Ni$_5$Zn$_{21}$. Ethane is produced from both acetylene ($^{13}$C$_2$H$_6$) and ethylene ($^{12}$C$_2$H$_6$) in approximately a 1:3 ratio regardless of zinc content. Since the ratio of acetylene to ethylene in the gas-phase is less than 1:20 as the reaction proceeds, it is clear that ethane is being produced directly from ethylene that remains on the surface after being produced from acetylene. Since acetylene binds much more strongly to the catalyst surface than ethylene, the surface is primarily covered with acetylene. This explains why the rate of $^{12}$C$_2$H$_6$ formation is low during the majority of the reaction. At high acetylene conversions, the rate of $^{12}$C$_2$H$_6$ formation increases as the sites become available for ethylene to adsorb and react on the surface. The formation of $^{13}$C$_2$H$_4$ increases with increasing Zn content, with Ni$_5$Zn$_{21}$ demonstrating a significantly higher selectivity to $^{13}$C$_2$H$_4$ than the other catalysts tested. The approximate turnover frequencies (TOF) for Ni, Ni$_4$Zn, NiZn, and Ni$_5$Zn$_{21}$ are $2\times10^{-2}$, $9\times10^{-3}$, $1\times10^{-3}$, and $2\times10^{-4}$ s$^{-1}$, respectively. Rates on a gravimetric basis are shown in Table S2-1 of the supplementary information. TOF is defined as acetylene consumption per surface Ni atom per
second. The Ni surface area is approximated as the mole fraction Ni in the sample times the total surface area. The atomic surface density for Ni is approximated using the surface density of the Ni(111) facet. Total surface areas were determined by BET surface area measurements (Table S2-1 of the supplementary information).
Figure 2-2. Catalytic behavior for Ni (A), Ni$_2$Zn (B), NiZn (C), and Ni$_5$Zn$_{21}$ (D) during the hydrogenation of a mixture of $^{13}$C$_2$H$_2$ and $^{12}$C$_2$H$_4$ at 160 °C in a batch reactor. Initial partial pressures of $^{13}$C$_2$H$_2$, H$_2$, and $^{12}$C$_2$H$_4$ were ~2.5 Torr, 27 Torr, and 53 Torr, respectively. The first two data points of each data set are at room temperature, prior to heating. The vertical line indicates the point at which the reactor reached 160 °C. Three- and four-carbon species are shown in Figure S2-3 of the supplementary information.
The overall ethylene selectivity (defined in eq 1) as a function of acetylene conversion for each of the Ni-Zn catalysts is shown in Figure 2-3. The low ethylene selectivity for Ni may be attributed to a high selectivity to both oligomeric species and ethane formation. The decrease in ethylene selectivity at high acetylene conversion is a result of an increase in gas-phase ethylene adsorption and subsequent reaction. Ni$_2$Zn and NiZn exhibit similar ethylene selectivity across the entire range of acetylene conversion. The ethylene selectivity for Ni$_3$Zn$_{21}$ is substantially higher than the other catalysts tested.

The product of acetylene semi-hydrogenation, $^{13}$C$_2$H$_4$, as a function of acetylene conversion, is shown in Figure 2-4. The overall increase in ethylene selectivity with increasing Zn content may be primarily attributed to an increased rate of $^{13}$C$_2$H$_4$ production. The selectivity to labeled ethane ($^{13}$C$_2$H$_6$) is shown in Figure 2-5 and is similar across the series of catalysts; $^{13}$C$_2$H$_6$ is not a major product as it represents less than 5% of the total $^{13}$C product. Thus, for both pure Ni and for the Ni-Zn catalysts, the majority of ethylene produced is desorbed from the surface, without further hydrogenation to produce ethane. The $^{13}$C$_2$H$_6$ is produced sequentially from $^{13}$C$_2$H$_2$, without ethylene desorption. This is clear because the concentration of gas-phase $^{13}$C$_2$H$_4$ is always at least 20 times less than the concentration of gas-phase $^{12}$C$_2$H$_4$ based on the initial concentrations of $^{13}$C$_2$H$_2$ and $^{12}$C$_2$H$_4$. Production of both ethylene and ethane from acetylene is constant across acetylene conversion which shows that the distribution of hydrogenation products of acetylene is insensitive to the concentration of gas-phase acetylene. The gas-phase concentrations of the other reactants, ethylene and hydrogen, remain approximately constant over the course of the reaction since the reaction is run with dilute acetylene.
Figure 2-3. Ethylene selectivity during the selective hydrogenation of acetylene in the presence of ethylene for Ni, Ni$_4$Zn, NiZn, and Ni$_5$Zn$_{21}$ in a batch reactor at 160 °C. Initial partial pressures of $^{13}$C$_2$H$_2$, H$_2$, and $^{12}$C$_2$H$_4$ were ~2.5 Torr, 27 Torr, and 53 Torr, respectively. Ethylene selectivity is defined as the net ethylene production per acetylene removal (eq 1).
Figure 2-4. $^{13}$C$_2$H$_4$ mole fraction as a function of $^{13}$C$_2$H$_2$ conversion during acetylene hydrogenation in the presence of ethylene in a batch reactor at 160 °C. Initial partial pressures of $^{15}$C$_2$H$_2$, H$_2$, and $^{12}$C$_2$H$_4$ were ~2.5 Torr, 27 Torr, and 53 Torr, respectively.
Since we only quantified the amount of $C_2$-$C_4$ products, a carbon balance was used to determine the amount of products with 5 or more carbon atoms in a molecule. The oligomer selectivity is defined as the sum of the selectivity to all species with 3 or more carbon atoms and is normalized with respect to carbon atoms such that acetylene conversion and oligomer selectivity may be directly compared. Previous research has shown that acetylene semi-hydrogenation on nickel catalysts produces a broad range of oligomeric products, primarily in the $C_3$-$C_{10}$ range [26]. Even-numbered products are predominant, resulting from the addition of $n$ C$_2$ acetylene while odd-numbered products (i.e. propylene) are likely the result of fragmentation of bound even-numbered carbon species [26]. The oligomer selectivity as a function of acetylene conversion is shown in Figure 2-5. The oligomer selectivity increases monotonically with increasing Ni content, with pure Ni producing the highest fraction of oligomers and Ni$_5$Zn$_{21}$ producing substantially less oligomers than all other compositions. The most significant impact of Zn inclusion is to lower the propensity for carbon-carbon bond formation.
Figure 2-5. Oligomer selectivity (defined as three or more carbons in a molecule) and $^{13}$C$_2$H$_6$ selectivity as a function of acetylene conversion during acetylene hydrogenation in the presence of ethylene in a batch reactor at 160 °C. Initial partial pressures of $^{13}$C$_2$H$_2$, H$_2$, and $^{12}$C$_2$H$_4$ were ~2.5 Torr, 27 Torr, and 53 Torr, respectively.
Butadiene is produced from the oligomerization of two acetylene molecules. Contrary to the other acetylene-derived products, butadiene selectivity does not remain constant for any of the catalysts tested (Figure 2-6). The selectivity to butadiene decreases with increasing acetylene conversion. For Ni\textsubscript{5}Zn\textsubscript{21}, the butadiene selectivity decreases significantly at high acetylene conversions. This demonstrates that butadiene is being consumed by a secondary reaction. Butadiene is likely the precursor for higher molecular weight carbon species via a reaction with acetylene\textsuperscript{26}. However, another secondary reaction of butadiene is the hydrogenation to a monounsaturated butene isomer. Ni\textsubscript{5}Zn\textsubscript{21} produces substantially more butadiene than the other catalysts, which may be a result of a decreased binding energy and a lower propensity for butadiene to remain on the catalyst surface and continue to react to form higher molecular weight oligomers. The mole fractions of the other gas-phase oligomerization products that were quantified are shown in Figure S2-3 of the supplementary information.
Figure 2-6. Butadiene selectivity as a function of acetylene conversion during acetylene hydrogenation in the presence of ethylene in a batch reactor at 160 °C. Initial partial pressures of $^{13}$C$_2$H$_2$, H$_2$, and $^{12}$C$_2$H$_4$ were ~2.5 Torr, 27 Torr, and 53 Torr, respectively. Data for acetylene conversions < 0.01 not included due to the high error associated with these points.
2.3.3. Analysis of the Reaction Energy Diagrams for Hydrogenation and Oligomerization

To gain insight into the reason for the enhanced selectivity of Ni-Zn catalysts, we calculated the energetics of the hydrogenation and oligomerization of acetylene on Ni(111) and intermetallic NiZn(101). The DFT calculated reaction energy diagram for the hydrogenation of acetylene is shown in Figure 2-7 and structures of extrema along the reaction coordinate are shown in Figures S2-3 and S2-4. The reaction begins with the adsorption of acetylene, adsorption of hydrogen, and reaction to form C₂H₃* (vinyl). C₂H₃* reacts with a second adsorbed hydrogen atom to form C₂H₄ (ethylene). Adsorbed ethylene may either desorb to form gas-phase ethylene, or it may react further to form ethane. A primary difference between Ni and NiZn is the relative adsorption energy of acetylene and ethylene. The adsorption energy of acetylene on Ni is -2.37 eV, compared to -1.36 eV on NiZn. The adsorption energies of ethylene on Ni and NiZn are -0.73 eV and -0.40 eV, respectively. The addition of zinc to nickel significantly reduces the ability of acetylene to bind strongly to the surface. This result is consistent with an experimentally observed decrease in turnover frequency and increase in the apparent reaction order in acetylene with increasing zinc content.

The competing pathway to acetylene hydrogenation is oligomerization. We pay particular attention to this pathway, as experimentally it is largely influenced by the addition of zinc. Previous work has suggested that oligomerization on Ni occurs through carbon-carbon bond formation of adsorbed acetylene and vinyl according to Scheme 2.
Scheme 2-2. Proposed mechanism of acetylene oligomerization. C$_2$H$_2$ is partially hydrogenated to form C$_2$H$_3$ which reacts with adsorbed C$_2$H$_2$ to form C$_4$H$_5$.\(^a\)

\(^a\)Dashed lines correspond to bonds to the catalyst surface.
Figure 2-7. DFT calculated reaction energy diagram for the hydrogenation of acetylene on Ni(111) and NiZn(101) surfaces. Energies are relative to the sum of a bare surface, gas-phase acetylene, and two gas-phase hydrogen molecules.
The reaction energetics for Scheme 2 were calculated on Ni(111) and NiZn(101) and are presented in Figure 2-8. Structures of extrema along the oligomerization path are shown in Figures S2-5 and S2-6. The reaction path begins with the partial hydrogenation of acetylene to form an adsorbed vinyl. Vinyl and adsorbed acetylene react to form C\textsubscript{4}H\textsubscript{5}. C\textsubscript{4}H\textsubscript{5} and an adsorbed hydrogen atom react to form butadiene, C\textsubscript{4}H\textsubscript{6}. It is also possible to form 1-butene, cis-2-butene, and trans-2-butene, depending on the hydrogen availability. Butadiene may subsequently desorb from the surface or further react with acetylene to form higher molecular weight oligomers. The activation barrier for carbon-carbon bond formation is 0.92 eV on Ni and 0.39 eV on NiZn. While the barrier for carbon-carbon bond formation on NiZn is significantly lower than pure Ni, we show in the Discussion section that the surface coverage of reactants must be considered when analyzing the reaction kinetics. Analysis using Langmuir-Hinshelwood kinetics will show that the addition of Zn reduces the selectivity of the catalyst to oligomerization products.
Figure 2-8. Theoretical reaction energy diagram calculated with DFT for the oligomerization of acetylene on Ni(111) and NiZn(101) surfaces. The proposed mechanism for oligomerization involves the addition of one hydrogen atom to an adsorbed acetylene molecule to form an adsorbed $\text{C}_2\text{H}_3^*$ followed by carbon bond formation with another adsorbed acetylene molecule followed by addition of a hydrogen atom to create butadiene. Energy is relative to a bare surface, two gas-phase acetylene molecules, and one gas-phase hydrogen molecule.
Figure 2-8 shows a high activation barrier for C₄H₅ hydrogenation on NiZn(101). This results from the difficulty in adding a hydrogen along the lines of Ni atoms on the NiZn(101) surface (see Figure S2-7). This result is highly dependent on the chosen NiZn surface and would be different if the surface exposed less well-ordered NiZn arrangements, whereas all other Ni vs. NiZn differences are indicative of shorter range Zn substitutinal effects. Figure 2-9 shows the transition states for vinyl hydrogenation and C-C bond formation on Ni and NiZn.
Figure 2-9. Transition states for vinyl hydrogenation and C-C bond formation on Ni(111) (A,B) and NiZn(101) (C,D), respectively. Ni atoms are light pink and Zn atoms are dark blue.
2.4. Discussion

The bulk synthesis of the intermetallic Ni-Zn compounds yields well-defined structures that are not easily attainable (or detectable) using conventional supported-catalyst syntheses. Each of the catalysts contain a unique Ni coordination environment. Pure Ni has 12 nearest Ni neighbors, while Ni$_4$Zn has, on average, 2.4 of these Ni neighbors replaced by Zn atoms. The Ni in intermetallic NiZn is coordinated by exactly 8 nearest Zn neighbors, with 6 Ni atoms slightly further away. The Ni in intermetallic Ni$_5$Zn$_{21}$ is special in that it has only Zn neighbors in an ideal structure. During and after the milling process, the catalysts were not subjected to air or high temperatures, which reduces the likelihood of the surface composition deviating significantly from the bulk. The energy penalty for segregation of Ni and Zn to the surface of intermetallic NiZn is 1.23 and 0.33 eV, respectively. Thus, there is a significant barrier for segregation of either Ni or Zn to the surface of the catalysts.

Table 2-2 shows a comparison of ethylene and ethane selectivities between the present work and other similar studies of Ni and Ni-Zn catalysts reported in the literature. We find that ethane selectivity decreases slightly with increasing Zn content, which is in agreement with the literature. However, we do not observe a 100-fold decrease as reported by Studt et al. We hypothesize that the 2.5% Ni, 7.5% Zn/MgAl$_2$O$_4$ catalyst of Studt et al. with extremely low ethane selectivity is controlled by ZnO, rather than intermetallic NiZn. Following similar preparation methods to that of Studt et al., Trimm and co-workers reported ZnO remains after reduction and found no evidence for intermetallic NiZn formation. Since no reaction temperature is reported in the study of Studt et al., it is possible that ZnO selectively removed acetylene at high temperature, producing oligomeric products instead of both ethylene and ethane.

We have shown direct measurement of ethylene selectivity is the best descriptor of catalytic performance. Without using isotopic labeling, it is very difficult to measure ethylene selectivity
since the reaction is run with excess ethylene. The ethane selectivities reported here are similar to the work of Trimm et al.²⁰,²⁷.

### Table 2-2. Summary of ethylene and ethane selectivities over nickel and nickel-zinc catalysts.a

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Selectivities</th>
<th>Reactants</th>
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<th>Reference</th>
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<td>d</td>
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<tr>
<td>4.5% Ni/Zn/MgAl2O4</td>
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<td>18</td>
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<td>36</td>
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<tr>
<td>2.5% Ni/Zn/MgAl2O4</td>
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<td>&lt;</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>2% Ni/SiO2</td>
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<td>13</td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>2% Ni/MgAl2O4</td>
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<tr>
<td>0.7% Ni/Zn/MgAl2O4</td>
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<tr>
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<td>53</td>
<td>10</td>
<td>160</td>
<td>Present work</td>
</tr>
</tbody>
</table>

aAll selectivities are reported at an acetylene conversion of 75%. bEthylene selectivity defined in Eq 1. For the case where ethylene is not present in the reactant mixture, ethylene selectivity is defined as moles of ethylene production per mole of acetylene consumption. cEthane selectivity defined as moles of ethane production per mole of acetylene consumption. dEthylene selectivity not determined by Studt et al. eTemperature not reported by Studt et al.
Most significant is our finding that ethylene selectivity is highly dependent on zinc content. The ethylene selectivity increases monotonically with increasing Zn content, with Ni$_4$Zn$_{21}$ exhibiting the highest ethylene selectivity. Trimm et al. observed an increase in ethylene selectivity for acetylene only hydrogenation using 0.7% Ni, 1.5% Zn/MgAl$_2$O$_4$ over that of a 2% Ni/MgAl$_2$O$_4$ catalyst. Ethylene selectivity was not determined in the study of Studt et al. because of the difficulty in measuring ethylene selectivity in excess ethylene without the use of isotopic labeling.

We find the observed increase in ethylene selectivity with Zn inclusion may be attributed primarily to a decrease in the production of oligomers. A similar effect has been observed for mixed Cu-Ni-Fe oxides for the semi-hydrogenation of propyne to propene. The addition of Ni to Cu-based catalysts increases the ability of the catalyst to dissociate hydrogen and ultimately minimize oligomerization. In addition, the isolation effect of adding Ni to Cu has been shown to improve the resistance to oligomerization. Similarly, for Ni-Al mixed oxides derived from takovite, the maximum in propene selectivity is a result of the optimization of hydrogenation and oligomerization.

The influence of zinc content is explained in terms of structure. The number of nearest Ni neighbors for Ni, Ni$_4$Zn, NiZn, and Ni$_2$Zn$_{21}$ are 12, 9.6, 6, and 0, respectively. Isolation of Ni atoms with Zn alters the ability of C$_2$H$_2$ to adsorb and react to form oligomers. We use DFT to provide additional insight into the reason for the enhanced ethylene selectivity. Previous research using DFT to study Ni-Zn catalysts only provided a qualitative assessment of the hydrogenation reaction energy diagram. Considering the activation barrier for carbon-carbon bond formation alone, our results from DFT would suggest that carbon-carbon bond formation is more facile on NiZn. However, with a large change in the acetylene adsorption strength on Zn-containing catalysts, the surface coverage will change significantly. Therefore, we use Langmuir-Hinshelwood kinetics to model the surface coverage and reaction. It is assumed that the adsorption of acetylene, hydrogen, and ethylene take place on the same kind of active site. On a
2x2 Ni(111) surface with one acetylene molecule, the addition of 2 H atoms results in an increase in hydrogen adsorption energy of 0.38 eV per hydrogen atom compared to hydrogen adsorption on an empty surface. This repulsive interaction suggests H cannot adsorb on “interstitial” sites of a surface with high acetylene coverage, supporting the assumption that hydrogen occupies the same active site as acetylene and ethylene.

We pay particular attention to the competition between oligomerization and hydrogenation. The oligomerization selectivity \( S_{\text{olig}} \) is derived in the supplementary information, with the result shown in eq 4.

\[
S_{\text{olig}} = \frac{\text{rate of vinyl hydrogenation}}{\text{rate of vinyl oligomerization}} = \frac{k_{C_2H_3} \theta_{C_2H_3} \theta_H}{k_{C-C} \theta_{C_2H_3} \theta_{C_2H_2}} \quad (4)
\]

The rate of vinyl hydrogenation is the product of the rate constant for adding a hydrogen to \( C_2H_3 \) \( (k_{C_2H_3}) \), the surface coverage of hydrogen \( (\theta_H) \), and the surface coverage of \( C_2H_3 \) \( (\theta_{C_2H_3}) \). The rate of vinyl oligomerization is defined as the product of the rate constant for carbon-carbon bond formation \( (k_{C-C}) \), the surface coverage of \( C_2H_3 \) \( (\theta_{C_2H_3}) \), and the surface coverage of \( C_2H_2 \) \( (\theta_{C_2H_2}) \). Included in the rate constants are pre-exponential factors and exponential terms (Arrhenius form) which include the activation energies \( E_{a,C_2H_3} \) and \( E_{a,C-C} \) for \( C_2H_3 \) hydrogenation and carbon-carbon bond formation, respectively. The surface coverage terms \( \theta_{C_2H_2} \) and \( \theta_H \) are determined from the adsorption energy of \( C_2H_2 \) \( (\Delta E_{ads,C_2H_2}) \) and H \( (\Delta E_{ads,H}) \), respectively, and a site balance.

We compare the selectivity of Ni(111) and NiZn(101) using the relevant adsorption energies and transition state energies from the reaction energy diagrams in Figures 2-7 and 2-8 (Table 2-3). Pre-exponential terms are assumed to be approximately constant for both Ni and NiZn. This gives rise to the expression in eq 5.
\[
\frac{S_{\text{oligNI}}}{S_{\text{oligNIzN}}} = \left( \frac{e^{\frac{\Delta E_{\text{ads,C}_2H_2} + E_{a,c,c} - \Delta E_{\text{ads,H}} - E_{a,c_2H_2}}{kT}}}{e^{\frac{\Delta E_{\text{ads,C}_2H_2} + E_{a,c,c} - \Delta E_{\text{ads,H}} - E_{a,c_2H_2}}{kT}}} \right)_{\text{Ni}}^{\text{NiZn}}
\]
Table 2-3. Relevant activation barriers and adsorption energies for calculation of ethylene selectivity.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E_{\text{ads},C_2H_2}$</th>
<th>$\Delta E_{\text{ads},H}$</th>
<th>$E_{a,C-C}$</th>
<th>$E_{a,C_2H_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (111)</td>
<td>-2.37</td>
<td>-0.46</td>
<td>0.92</td>
<td>0.51</td>
</tr>
<tr>
<td>NiZn (101)</td>
<td>-1.36</td>
<td>-0.47</td>
<td>0.39</td>
<td>0.46</td>
</tr>
</tbody>
</table>
The most significant difference between the energies presented in Table 2-3 is the difference in adsorption energy of acetylene on Ni and NiZn. Eq 5 predicts that NiZn will have an $S_{\text{olig}}$ that is $\sim 10^6$ higher than Ni. According to eq 5, stronger acetylene adsorption corresponds to a decrease in ethylene selectivity due to the promotion of oligomerization of acetylene. The reduction in the binding strength of acetylene on NiZn allows for the hydrogenation of acetylene rather than oligomerization. Thus, DFT provides a reason for experimentally-observed enhanced selectivity with increasing Zn content. The addition of Zn to Ni results in a lower adsorption strength for acetylene, a lower coverage of acetylene on the surface, and ultimately a lower propensity for carbon-carbon bond formation. This causes more acetylene to be hydrogenated to form ethylene. While DFT correctly predicts NiZn will have a lower oligomerization selectivity than Ni, the magnitude of the difference is much larger than what is observed experimentally. We attribute this to the simplifications made in the DFT modeling. One simplification is that the adsorption energies and activation barriers are assumed to be coverage-independent. However, it is well known there is strong coverage dependence on adsorption energies $^{51-53}$. For example, previous research has shown the adsorption energy for O on Pt(111) varies from -0.79 eV at a coverage of 0.25 monolayer to -0.5 eV at a coverage of 0.5 monolayer $^{52}$. Taking into account the coverage dependence of adsorption energies may help to provide a more quantitative description of the selectivities for Ni and NiZn.

The ethylene selectivity of bulk Pd$_{20}$Ag$_{80}$ for acetylene semi-hydrogenation in the presence of excess ethylene was found to be 49% by Osswald and coworkers $^{16}$. This selectivity is comparable with the ethylene selectivity for bulk Ni$_5$Zn$_{21}$ determined in the present study. The ethylene selectivity for alumina-supported Pd-Ag catalysts has been reported to vary from -27% to 78% $^{54,55}$; however, ethylene selectivity is highly dependent on acetylene conversion and reaction conditions which makes a direct comparison difficult. Pd-Ag and Ni$_5$Zn$_{21}$ become differentiated in terms of the minority products of the reaction. The second most prevalent product over a Pd-Ag catalyst is ethane, while Ni$_5$Zn$_{21}$ produces very little ethane. Instead,
Ni_{5}Zn_{21} converts ~40% of the starting acetylene to oligomers. The result is that Ni-based catalysts will deactivate over time, while Pd-based catalysts will not. A prime example of a stable and selective catalyst is intermetallic PdGa\textsuperscript{13-17}. PdGa achieves high stability through covalent interactions between Pd and Ga. Isolation of the Pd atoms in the Ga matrix results in a catalyst that is both selective and active for acetylene semi-hydrogenation in the presence of ethylene.
2.5. Conclusions

In this work, we measured ethylene selectivity during acetylene semi-hydrogenation in the presence of excess ethylene using isotopic labeling in a batch reactor. Ethane is produced from both acetylene and ethylene, while oligomeric species are produced from acetylene only. Contrary to previous reports, the production of ethane is not highly dependent on zinc content for Ni-Zn catalysts with well-defined intermetallic structures. However, the addition of Zn to Ni serves to reduce the selectivity to oligomeric species produced from acetylene. DFT calculations show the reason for the reduction in carbon-carbon bond formation on NiZn is a decrease in the adsorption energy and resultant surface coverage of acetylene. Langmuir-Hinshelwood kinetics demonstrates differences in surface coverage on Ni and NiZn which ultimately lead to the enhanced selectivity of NiZn. Practical use of Ni-based catalysts is limited by their ability to reduce carbon-carbon bond formation and prevent "green oil" buildup, which leads to eventual catalyst deactivation. The enhanced selectivity of Ni$_5$Zn$_{21}$ compared to pure Ni is at the expense of a significant reduction in turnover frequency. Additionally, synthesis of supported catalysts with the γ-Brass Ni-Zn phase (e.g. Ni$_5$Zn$_{21}$) may be impossible due to the high vapor pressure of zinc at elevated temperatures and its oxophilic nature. Other base metal combinations including NiSn, NiGa, CoGa, and FeZn have been proposed as viable alternatives to Pd-based catalysts, but have not yet been studied in detail. Further work with base-metal catalysts may prove useful in finding active and selective replacements for Pd-based hydrogenation catalysts.
2.6. References


2.7. Supplementary Information

2.7.1. Supplementary Tables and Figures

Figure S2-1. Ni-Zn phase diagram reproduced with permission from P. Nash and Y. Y. Pan, 1987.
Figure S2. SEM images of Ni (A), Ni$_4$Zn (B), NiZn (C), and Ni$_{19}$Zn$_{21}$ (D) as synthesized. Scale bar is 100 μm.
Table S2-1. Reaction rates and turnover frequencies for bulk Ni-Zn catalysts.

| Catalyst | Mass (mg) | Surface Area (m²/g)
<table>
<thead>
<tr>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>25</td>
<td>0.093</td>
</tr>
<tr>
<td>Ni₂Zn</td>
<td>25</td>
<td>0.14</td>
</tr>
<tr>
<td>NiZn</td>
<td>40</td>
<td>0.38</td>
</tr>
<tr>
<td>Ni₅Zn₂₁</td>
<td>500</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction Rate (mol C₂H₂ g⁻¹ cat⁻¹ s⁻¹)</td>
<td>TOF (1/s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>9.5 × 10⁹</td>
<td>3.8 × 10⁻³</td>
</tr>
<tr>
<td>Ni₂Zn</td>
<td>1.8 × 10⁻⁸</td>
<td>6.1 × 10⁻³</td>
</tr>
<tr>
<td>NiZn</td>
<td>5.5 × 10⁻⁹</td>
<td>1.1 × 10⁻³</td>
</tr>
<tr>
<td>Ni₅Zn₂₁</td>
<td>7.7 × 10⁻¹⁰</td>
<td>2.0 × 10⁴</td>
</tr>
</tbody>
</table>

*Turnover frequency calculation performed under the approximation the Ni surface area is the mole fraction Ni in the sample times the total surface area, using a Ni atomic area of 6.21 Å².

*Surface area determined from N₂ BET.
Figure S2.3. Propylene, 1-butene, cis-2-butene, isobutylene, and trans-2-butene mole fraction as a function of acetylene conversion for Ni (A), Ni$_2$Zn (B), NiZn (C), and Ni$_5$Zn$_{21}$ (D).
Figure S2-4. Structures of each extrema for the hydrogenation pathway on Ni(111). Adsorbed acetylene and hydrogen (A) react (transition state shown in B) to form adsorbed C$_2$H$_3$ (C). Adsorbed C$_2$H$_3$ and hydrogen (D) react (transition state shown in E) to form adsorbed ethylene (F). Adsorbed ethylene and hydrogen (G) react (transition state shown in H) to form adsorbed C$_2$H$_5$ (I). Finally, adsorbed C$_2$H$_5$ and hydrogen (J) react (transition state shown in K) to form adsorbed ethane (L). Two hydrogen atoms of ethane are pointed down towards the nickel surface in L.
Figure S2-5. Structures of each extrema for the hydrogenation pathway on NiZn(101). Adsorbed acetylene and hydrogen (A) react (transition state shown in B) to form adsorbed C$_2$H$_3$ (C). Adsorbed C$_2$H$_3$ and hydrogen (D) react (transition state shown in E) to form adsorbed ethylene (F). Adsorbed ethylene and hydrogen (G) react (transition state shown in H) to form adsorbed C$_2$H$_5$ (I). Finally, adsorbed C$_2$H$_5$ and hydrogen (J) react (transition state shown in K) to form adsorbed ethane (L).
Figure S2-6. Structures of each extrema for the oligomerization pathway on Ni(111). Adsorbed acetylene and hydrogen (A) react (transition state shown in B) to form adsorbed C$_2$H$_3$ (C). Adsorbed C$_2$H$_3$ and acetylene (D) react (transition state shown in E) to form adsorbed C$_4$H$_5$ (F). Adsorbed C$_4$H$_5$ and hydrogen (G) react (transition state shown in H) to form adsorbed butadiene, C$_4$H$_6$ (I).
Figure S2-7. Structures of each extrema for the oligomerization pathway on NiZn(101). Adsorbed acetylene and hydrogen (A) react (transition state shown in B) to form adsorbed C$_2$H$_3$ (C). Adsorbed C$_2$H$_3$ and acetylene (D) react (transition state shown in E) to form adsorbed C$_4$H$_5$ (F). Adsorbed C$_4$H$_5$ and hydrogen (G) react (transition state shown in H) to form adsorbed butadiene, C$_4$H$_6$ (I).
2.7.2. Derivation of the oligomerization selectivity, $S_{\text{olig}}$ using Langmuir-Hinshelwood kinetics

The oligomerization selectivity is defined as the rate of vinyl hydrogenation divided by the rate of vinyl oligomerization, shown below. The rate of vinyl hydrogenation is a product of the surface fraction of vinyl ($\Theta_{\text{C}_2\text{H}_3}$), the surface fraction of hydrogen ($\Theta_{\text{H}}$), and the rate constant for vinyl hydrogenation ($k_{\text{C}_2\text{H}_3}$). The rate of vinyl oligomerization is a product of $\Theta_{\text{C}_2\text{H}_3}$, the surface fraction of acetylene ($\Theta_{\text{C}_2\text{H}_2}$), and the rate constant for carbon-carbon bond formation ($k_{\text{C-C}}$).

$$S_{\text{olig}} = \frac{\text{rate of vinyl hydrogenation}}{\text{rate of vinyl oligomerization}} = \frac{k_{\text{C}_2\text{H}_3} \Theta_{\text{C}_2\text{H}_3} \Theta_{\text{H}}}{k_{\text{C-C}} \Theta_{\text{C}_2\text{H}_3} \Theta_{\text{C}_2\text{H}_2}}$$

The site balance is shown below, where $\Theta_*$ is the surface fraction of empty sites.

$$1 = \Theta_{\text{C}_2\text{H}_2} + \Theta_{\text{H}} + \Theta_{\text{C}_2\text{H}_4} + \Theta_*$$

The equilibrium adsorption constants, $K_x$, are shown for acetylene, hydrogen, and ethylene below.

$$\Theta_{\text{C}_2\text{H}_2} = K_{\text{C}_2\text{H}_2} P_{\text{C}_2\text{H}_2} \Theta_*, \quad \Theta_{\text{H}} = K_{\text{H}} \sqrt{P_{\text{H}_2}} \Theta_*, \quad \Theta_{\text{C}_2\text{H}_4} = K_{\text{C}_2\text{H}_4} P_{\text{C}_2\text{H}_4} \Theta_*$$

$$\Theta_* = \frac{1}{K_{\text{C}_2\text{H}_2} P_{\text{C}_2\text{H}_2} + K_{\text{H}} \sqrt{P_{\text{H}_2}} + K_{\text{C}_2\text{H}_4} P_{\text{C}_2\text{H}_4} + 1} \equiv \frac{1}{A}$$

$$\Theta_{\text{C}_2\text{H}_2} = \frac{K_{\text{C}_2\text{H}_2} P_{\text{C}_2\text{H}_2}}{A}, \quad \Theta_{\text{H}} = \frac{K_{\text{H}} \sqrt{P_{\text{H}_2}}}{A}, \quad \Theta_{\text{C}_2\text{H}_4} = \frac{K_{\text{C}_2\text{H}_4} P_{\text{C}_2\text{H}_4}}{A}$$

Substitution into the equation for oligomerization selectivity yields the expression shown below.

$$S_{\text{olig}} = \frac{K_{\text{H}} \sqrt{P_{\text{H}_2}} k_{\text{C}_2\text{H}_3}}{K_{\text{C}_2\text{H}_2} P_{\text{C}_2\text{H}_2} k_{\text{C-C}}}$$

The expressions for the equilibrium adsorption constants and rate constants are shown below where constant terms (including entropy) are lumped together into $A_1$, $A_2$, $A_3$, and $A_4$.

$$K_{\text{C}_2\text{H}_2} = A_1 e^{\Delta F_{\text{ads,C}_2\text{H}_2}/kT}, \quad K_{\text{H}} = A_2 e^{\Delta F_{\text{ads,H}}/kT}$$
Substitution into the equation for oligomerization selectivity yields the expression shown below.

\[ k_{C_2H_3} = A_3 e^{-\frac{E_{a,C_2H_3}}{kT}} \quad k_{C-C} = A_4 e^{-\frac{E_{a,C-C}}{kT}} \]

Dividing the oligomerization selectivities for Ni and NiZn yields an expression with only parameters calculated from the reaction energy diagram. The \( A_1-A_4 \) terms were cancelled under the assumption that they are approximately equal for Ni and NiZn.

\[
\frac{S_{\text{olig}}}{S_{\text{olig}}^\text{NiZn}} = \frac{\left( e^{-\frac{\Delta E_{\text{ads},C_2H_2} + E_{a,C-C} - \Delta E_{\text{ads},H} - E_{a,C_2H_2}}{kT}} \right)_\text{Ni}}{\left( e^{-\frac{\Delta E_{\text{ads},C_2H_2} + E_{a,C-C} - \Delta E_{\text{ads},H} - E_{a,C_2H_2}}{kT}} \right)_\text{NiZn}}
\]

\[
\frac{S_{\text{olig}}^\text{Ni}}{S_{\text{olig}}^\text{NiZn}} = \frac{e^{-\frac{-2.37+0.92+0.46-0.51}{kT}}}{e^{-\frac{-1.36+0.39+0.47-0.46}{kT}}} = \frac{e^{-1.5}}{e^{-0.96}} = e^{-0.54}
\]

\[
k = 8.62 \times 10^{-5} \text{ eV} \text{ atom}^{-1}K \quad T = 433 K
\]

\[
\frac{S_{\text{olig}}^\text{Ni}}{S_{\text{olig}}^\text{NiZn}} = 5.21 \times 10^{-7}
\]
2.7.3. Evaluation of mass and heat transfer effects

To evaluate external mass transfer effects, we compared the recirculation rate of the batch reactor (>50 bed volumes per minute), to the time scale of the reaction (~100 min). Since the bed volume was replaced >5000 times over the course of the reaction, external heat and mass transfer effects are minimized.

Since non-porous bulk catalysts were used for this study, internal mass transfer effects will be small. As a quantitative demonstration of this, the Thiele modulus was calculated using the following equation for the entire catalyst plug (consisting of the bulk catalyst particles):

\[ \eta \phi^2 = \frac{-r_{A(\text{obs})} \times \rho_c \times R^2}{D_e \times C_{A_s}} \]

- \( r_A \) = reaction rate \( \approx 7 \times 10^{-10} \) kmol kg\(^{-1}\) cat s\(^{-1}\)
- \( \rho_c \) = bulk density of catalyst powder \( \approx 1 \times 10^3 \) kg m\(^{-3}\)
- \( R \) = particle size \( \approx 6 \times 10^{-7} \) m
- \( D_e \) = effective gas-phase diffusivity \( \approx 2 \times 10^{-5} \) m\(^2\) s\(^{-1}\)
- \( C_{A_s} \) = gas concentration of A at the catalyst surface \( \approx 1 \times 10^{-4} \) kmol m\(^{-3}\)
- \( \eta \) = internal effectiveness factor \( \approx 1 \)
- \( \phi \) = Thiele modulus

The resulting Thiele modulus is \( 1 \times 10^{-5} << 1 \) which demonstrates internal mass transfer effects are insignificant.
3.1. Introduction

The production of ethylene from steam cracking of naphtha generates acetylene impurities as a by-product typically at a level of 0.5 – 2%. Acetylene must be reduced to less than 5 ppm to prevent deactivation of the ethylene polymerization catalyst.\textsuperscript{1,2} Pd/Al\textsubscript{2}O\textsubscript{3} or Pd/SiO\textsubscript{2} with low metal loadings (ca. 0.5 %) is widely used for the upgrading of olefins, but does not provide sufficient selectivity to warrant use in acetylene hydrogenation as a result of over-hydrogenation to ethane and oligomer (“green oil”) formation.\textsuperscript{3,4} To achieve high ethylene selectivity, co-feeding of CO or modification of the catalyst with Ag is required. The addition of Ag to Pd decreases hydrogen coverage, resulting in a lower propensity for over-hydrogenation and ultimately higher ethylene selectivity.\textsuperscript{4,12} Since the first patent on Pd-Ag catalysts in 1957\textsuperscript{13}, Pd-Ag remains the optimal catalyst for this process. However, there has been recent interest to improve on the current technology in terms of both catalyst selectivity and cost. Intermetallic Pd-Ga compounds demonstrate an increased ethylene selectivity compared to Pd-Ag as a result of electronic modification and isolation of the active sites of Pd.\textsuperscript{14-18} However, since catalyst cost is still a concern, there is interest in replacing Pd-based catalysts with low-cost, earth-abundant elements.

Replacement of Pd with an active component from the late 3d transition metals such as Fe, Cu, or Ni poses unique challenges that can be overcome through the addition of a second metal. For example, Fe catalysts require a pressure of at least 50 bar and a temperature of 100 °C.
for the hydrogenation of unsaturated C-C bonds. Modification of Fe with Al to form intermetallic Al$_{13}$Fe$_4$ was recently shown to exhibit high selectivity for acetylene hydrogenation as a result of site-isolation and alteration of the electronic structure of Fe due to chemical bonding. Cu-based hydrogenation catalysts tend to form oligomerization products but have been made more selective through the addition of Ni which increases the catalyst’s ability to dissociate hydrogen. Ni-based catalysts suffer from both their ability to over-hydrogenate and their tendency to oligomerize alkynes. Studt et al. identified Ni-Zn using density functional theory (DFT) as a good alkyne semi-hydrogenation catalyst and provided experimental evidence that the addition of Zn to a supported Ni/MgAl$_2$O$_4$ catalyst reduces the formation of ethane during acetylene hydrogenation in the presence of excess ethylene; however, no measure of oligomerization or ethylene selectivity was presented in this study. Recent work from our group has shown that bulk intermetallic Ni-Zn compounds reduce the formation of oligomeric compounds as a result of a decreased binding energy of acetylene, thereby boosting the selectivity to ethylene. As a result of the low surface areas and correspondingly low acetylene-removal rates of the most selective bulk intermetallic Ni-Zn catalysts, there exists a need to create highly-dispersed Ni-Zn catalysts.

Synthesis of supported intermetallic Ni-Zn catalysts is difficult due to the oxophilic nature and volatility of Zn. ZnO does not reduce under the presence of hydrogen, and instead ZnO sublimes at temperatures of approximately 600 °C. Evidence for the formation of an intermetallic Ni-Zn compound was not reported in either of the previous studies using co-impregnation of Ni and Zn on a MgAl$_2$O$_4$ support. Similarly, Ni-Zn catalysts derived from hydrotalcite-like precursors show no evidence for the formation of intermetallic Ni-Zn compounds. Furthermore, the amount of reduced Ni is lower in Zn-containing catalysts compared to catalysts without Zn, which stresses the difficulty in creating intermetallic Ni-Zn from divalent precursors. However, using ZnO as a support for Cu results in the reduction of ZnO and formation of a Cu-Zn alloy with the face-centered cubic structure. Pd/ZnO and Pt/ZnO
catalysts promote the facile reduction of the ZnO support under hydrogen, forming intermetallic PdZn and PtZn, respectively. Applications for Ni/ZnO catalysts beyond selective hydrogenation include hydrodeoxygenation and hydrodearomatization, methanol and ethanol steam reforming, and hydrodesulfurization. Of these Ni/ZnO catalysts, neither alloy nor intermetallic formation was observed in two cases, while Ni-Zn alloy formation was observed in two cases, and intermetallic β1-NiZn was clearly identified by Petzold et al. However, in the study by Petzold and coworkers it is unclear whether the intermetallic NiZn phase formed during the reduction or reaction step.

Herein, we report X-ray absorption near-edge structure (XANES) characterization during the in situ reduction of Ni/ZnO catalysts prepared from wet impregnation of nickel nitrate on a moderate surface area (41 m²/g) ZnO support. The in situ characterization is combined with ex situ characterization to obtain a complete picture of the structure of the Ni/ZnO catalysts after the calcination and reduction steps. We measured the catalytic selectivity for acetylene semi-hydrogenation in excess ethylene and the activity for H-D exchange to understand the effect of alloy formation and the ZnO support on the catalytic properties of Ni/ZnO catalysts. The beneficial catalytic properties derived from the formation of intermetallic NiZn are offset by acetylene oligomerization on ZnO, leading to a poor catalyst for acetylene semi-hydrogenation.
3.2. Experimental

3.2.1. Synthesis of supported catalysts

Ni/ZnO catalysts were synthesized by dissolving Ni(NO$_3$)$_2$·6H$_2$O (Sigma Aldrich) in Milli-Q water and adding to nanoscale ZnO powder (NanoActive® ZnO, NanoScale Corp, Manhattan, KS) using the wet impregnation technique. In a representative synthesis of 2 wt. % Ni/ZnO, 0.5 g of Ni(NO$_3$)$_2$·6H$_2$O was dissolved in 7 mL Milli-Q water and added to 4.9 g of ZnO powder. Weight loadings are defined as the mass of Ni divided by the total mass of Ni and ZnO in the catalyst sample. Samples were dried for 12 h at 110 °C followed by calcination at 450 °C for 4 h. A 2 wt. % Ni/SiO$_2$ catalyst was prepared by dissolving 0.01 g Ni(NO$_3$)$_2$·6H$_2$O in 10 mL Milli-Q water and adding to 1 g of Cabot CAB-O-SIL HS-5 silica. The mixture was stirred thoroughly, dried at 110 °C for 12 h, and calcined at 450 °C for 4 h. Actual weight loadings for the Ni/ZnO samples were determined with ICP-OES using an aqua regia digestion (which dissolves both NiO and ZnO) and are 0.50 ± 0.02, 0.99 ± 0.04, 1.97 ± 0.04, 4.8 ± 0.2, and 9.8 ± 0.4 wt. % for the nominal 0.5, 1, 2, 5, and 10 wt. % catalysts, respectively.

3.2.2. Synthesis of bulk intermetallic compounds

Bulk intermetallic Ni-Zn compounds were synthesized as reference materials for X-ray absorption spectroscopy, following a previously reported procedure.²⁹ Ni powder (Sigma Aldrich, <150 μm, 99.999 %) and Zn granules (Sigma Aldrich, 3 mm diam, 99.99 %) were added to alumina crucibles (LSP Ceramics, 13 mm i.d.) in the correct stoichiometry and sealed in quartz tubes evacuated to 30 mTorr. Ni$_5$Zn$_{21}$ and NiZn and were heated at a rate of 10 °C/min to 700 °C, held for 24 h, and cooled to room temperature at a rate of 1 °C/min. Ni$_4$Zn was heated at a ramp rate of 10 °C/min to 900 °C, held for 24 h, and cooled to room temperature at a ramp rate of 3
°C/min. A stainless steel ball mill (SPEX Mixer/Mill, 8001 sample container) was used to mill the samples. Samples were loaded into the ball mill in an argon-filled glove box and 1 mL of 1,1,1,2,2,3,4,5,5,5 decafluoropentane (Vertrel XF, Dupont) per gram of sample was added to the milling container prior to milling for 4 h. After milling, the decafluoropentane was allowed to evaporate at room temperature. NiZn and Ni$_5$Zn$_{21}$ were resealed in evacuated quartz tubes and annealed at 500 °C for 7 days. X-ray diffraction of these compounds shows phase pure intermetallic compounds were synthesized.

3.2.3. In situ X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) measurements were performed at beamline X19A of the National Synchrotron Light Source (NSLS) at Brookhaven National Lab (Upton, NY). NiO, ZnO, Ni$_4$Zn, NiZn, and Ni$_5$Zn$_{21}$ standards were prepared by spreading powder on adhesive polyimide tape and folding such that the step height at the Ni K-edge (8333 eV) was ~1.0. Ex situ measurements of catalyst samples were performed on samples prepared either by spreading powder on adhesive polyimide tape or by hand pressing a 4 mm OD pellet into a stainless steel holder. In situ reduction was performed with a hand-pressed pellet of pure catalyst sample in a 4 mm OD stainless steel holder. The edge step for the 2 wt. % Ni/ZnO sample was ~0.4. The calculated total absorption for this sample is ~3 absorption lengths. A K-type thermocouple was inserted into a small hole in the stainless steel holder ~5 mm away from the catalyst pellet. The stainless steel holder was placed inside a 2.54 cm OD quartz tube sealed with polyimide film and Swagelok Ultra Torr fittings and equipped with an inlet and outlet for the passage of gases. The quartz tube was placed within a tube furnace with a programmable temperature controller. The catalyst pellet was placed at the center of the X-ray beam. Transmission geometry was used for all experiments. The incoming and outgoing X-ray beams were measured with ionization chambers placed before and after the sample. A reference Ni foil was placed between the
transmission and reference ionization chambers for measurements at the Ni K-edge. Data was acquired from 150 eV before the edge to 980 eV after the edge. The total time for a single scan was ~15 min. For the in situ reduction, the sample was heated from room temperature to 800 °C at a rate of 1.3 °C/min under a 50 mL/min flow of 5 % H₂ balanced with He. Since the temperature was changing over the course of each individual scan, the reported temperatures are the average temperature for each scan.

3.2.4. Ex situ laboratory X-ray diffraction

Powder X-ray diffraction (XRD) measurements were performed on a PANalytical Empyrean X-ray diffractometer using Cu Kα (λ=1.5418 Å) radiation. The powder samples were placed in the cavity of a silicon zero-background holder and leveled with a glass slide. The Empyrean is equipped with a PIXcel detector using scanning line mode detection and the diffractometer radius is 240 mm. Incident beam optics were configured with a ½° antiscatter slit, 10 mm beam mask, ¼° fixed divergence slit, and 0.04 rad soller slits. Diffracted beam optics were configured with 0.04 rad soller slits, a Ni beta-filter, and a ¼° anti-scatter slit. Survey diffractograms were acquired with a 2Θ step size of 0.025° with a range from 20 to 90° 2Θ. High resolution scans with a longer time step were collected from 39 to 46° 2Θ. The diffractometer is checked weekly by measuring the lattice parameter of a NIST 640d Si standard reference material. The deviation from the true lattice parameter of the standard is always less than 0.001 Å, and thus the error on lattice parameters determined from the XRD measurements is assumed to be less than 0.001 Å. The instrumental broadening parameter used in the Scherrer equation for calculation of particle size was determined from the diffraction pattern of the NIST 640d Si standard reference material. For determination of lattice parameters, Rietveld Refinement of the XRD data was performed within Jade (Materials Data Incorporated). The error estimate reported
for each lattice parameter is either the standard deviation in lattice parameter determined from Rietveld Refinement, or the instrumental accuracy (0.001 Å), whichever is greater.

3.2.5. Ex situ synchrotron X-ray diffraction and pair distribution function (PDF) analysis

Synchrotron X-ray diffraction and pair-distribution function analysis was performed at beamline 11-ID-B at the Advanced Photon Source (APS) at Argonne National Laboratory (Lemont, IL). Measurements were performed at room temperature with an X-ray wavelength of 0.2127 Å, a 0.2 × 0.2 mm X-ray beam size, and a Q_{max} of 24 Å^{-1}. Two-dimensional (2D) X-ray diffraction patterns were acquired with a General Electric amorphous silicon flat panel detector. Samples were prepared for analysis by filling a polyimide capillary (1 mm ID) and sealing with epoxy. The raw 2D X-ray data was integrated radially using FIT2D. The data were subsequently processed using PDFGetX2 to remove the background, normalize, and calculate the Fourier transform resulting in the PDF, G(r). The calcined catalyst samples were analyzed by subtracting the empty polyimide capillary PDF. Subsequently, the experimental PDF of pure calcined ZnO was subtracted from the sample PDF. This was done by first adjusting the ZnO PDF with a multiplier and a power expression, a*R^b, where a and b are fitted constants. This was done to account for different amounts of ZnO in each sample and particle sizes which differ from the reference spectrum. The grain sizes of the ZnO nanoparticles increased with increasing Ni weight loading requiring the power expression to subtract the ZnO contribution from each of the PDFs. The PDF for samples that were calcined and reduced were prepared in a similar manner. After subtraction, G(r) was fitted using PDFGUI with a NiO (NaCl structure) and Ni (FCC structure) phase for the calcined and reduced samples, respectively. ZnO was also fitted to each of the samples.
3.2.6. Temperature programmed reduction

Temperature programmed reduction (TPR) was performed using a Micromeritics AutoChem 2910. 300 mg of sample was added to a U-shaped quartz tube and supported with quartz wool. Samples were heated from room temperature to 600 °C at a rate of 10 °C/min under 3.88 % H₂ balanced with Ar at a flow rate of 50 mL/min. Hydrogen uptake was monitored using a thermal conductivity detector (TCD) based on the differences in thermal conductivity of hydrogen and argon. Calibration was performed by measuring the hydrogen uptake of a known amount of copper (II) oxide. The raw signal was converted to the rate of hydrogen consumption using the calibration and hydrogen flow rate.

3.2.7. Transmission electron microscopy

Samples were prepared for transmission electron microscopy (TEM) by sonicating the catalyst powders in ethanol and dropping onto a carbon-coated copper TEM grid. The reduced samples were prepared in a nitrogen-filled glove box with an oxygen level of less than 1 ppm and transferred to the TEM in a sealed plastic bag. The samples were exposed to atmospheric oxygen for approximately 1 min during sample loading. Diffraction contrast imaging was performed on a JEOL 2010F field emission TEM operated at 200 keV. High resolution TEM imaging (HRTEM) was performed using a FEI TITAN 3GS operated at 80 keV and 200 keV. Elemental maps were calculated from spectrum images recorded in scanning TEM (STEM) mode by electron energy-loss spectroscopy (EELS). Fourier transforms of high resolution images were used for phase identification from lattice plane distances.
3.2.8. Catalysis measurements

Catalytic selectivity for acetylene semi-hydrogenation in excess ethylene was determined using a batch reactor. A 2 wt. % Ni/ZnO (200 mg) or Ni/SiO₂ (15 mg) sample was loaded into a ½ in. o.d. quartz reactor tube, supported by a plug of quartz wool on both sides. Catalysts were reduced in the reactor prior to catalysis under a flow of 50 mL/min 3.88 % H₂/Ar by heating at a ramp rate of 10 °C/min to the desired temperature. After reaching the desired temperature, the samples were cooled to room temperature under flowing 3.88 % H₂/Ar. Complete details of the experimental protocol for the catalytic measurements may be found in prior work.²⁹ Briefly, the reactor was evacuated to a pressure of ~100 mTorr prior to admission of the reactants. ¹³C₂H₂ was added to the reactor with a needle valve to a pressure of ~ 5 Torr (the starting pressure of acetylene slightly varied and the actual starting pressure for each experiment may be read from starting acetylene pressure in each plot). Subsequently, 10 % H₂/He was added to the reactor to a pressure of 267 Torr, and 10 % C₂H₄/He was added to reach a final pressure of 800 Torr. Reactants were circulated at a flow rate of ~50-100 mL/min using a diaphragm circulation pump. Samples were removed from the reactor with a 50 μL gas tight syringe (Hamilton) and analyzed with a Shimadzu GCMS-QP2010 Ultra gas chromatograph (GC) equipped with a mass spectrometer (MS). After two samples were taken at room temperature to establish the initial concentration of acetylene, the reactor was heated to 160 °C over the course of 10 min.

H-D exchange experiments were performed in a ½ in o.d. plug flow reactor, using identical amounts of catalyst as in the acetylene semi-hydrogenation experiments. The catalysts were reduced under flowing H₂ (10 mL/min) and D₂ (10 mL/min) in the reactor and were cooled to room temperature under an equimolar flow of H₂ and D₂. This procedure ensures equal concentration of H and D on the catalyst surface prior to the H-D exchange measurements. The reactor was subsequently heated at a rate of 3 °C/min to obtain temperature dependence of the H-D exchange. The concentrations of H₂ and HD were measured every 3-4 min by removing 50 μL
samples with a syringe from the exit of the reactor and injecting into the mass spectrometer. Because the mass spectrometer uses He as a carrier gas, m/z = 4 could not be used to detect D₂ and a mole balance was used to calculate the amount of D₂ from the H₂ and HD concentrations.
3.3. Data analysis

Energy calibration of the XAS data was performed by aligning all scans with the reference foil (8333 eV for Ni K-edge) prior to further processing. The IFEFFIT package was used for data normalization and processing. Background removal was performed using an Rbkg of 1.0, k-weight of 2, pre-edge range of -150 to -30 eV, normalization range of 150 to 980 eV, and a spline range of 0 to 16 k for all samples. The X-ray absorption near-edge structure (XANES) region was selected for factor analysis since it is relatively insensitive to the temperature effects of the EXAFS Debye-Waller factor. The normalized XANES data from 8307 to 8399 eV were collected in a matrix and singular value decomposition was used to determine the eigenvalues and eigenvectors. To determine the number of principal components, the data were reconstructed with either two or three components and the residuals were plotted, following the method of Wang et al. Ideally, pure phases would be selected for linear combination fitting to determine the mixing fractions of species as a function of temperature. However, using room temperature reference spectra is not appropriate due to small changes in the XANES spectra at higher temperature. Therefore, iterative key set factor analysis (IKSFA) was used to determine which of the XANES data sets were most fundamental (i.e. best represent the entire data set through a linear combination of these data sets) and to select the intermediate spectra used for linear combination fitting of the data. IKSFA has been previously described in the literature for examining the intermediate state of Cu-ZSM-5 under reaction conditions. For calculation of R-space EXAFS data, a k-range of 2 to 13 and a k-weight of 2 was used for the Fourier transform.
3.4. Results

3.4.1. Structural and morphological properties of Ni/ZnO after calcination

XRD patterns of Ni/ZnO and Ni/SiO$_2$ after calcination are shown in Figure 3-1. After oxygen treatment (calcination in air at 450 °C for 4 h), the only phases observable with XRD are NiO (JCPDS Card no. 47-1049, NaCl structure) and ZnO (JCPDS card no. 36-1451, wurtzite structure) for the Ni/ZnO catalysts. A high resolution scan of the region from 39 to 46 °2Θ is shown in Figure 3-1 and complete scans are shown in Figure S3-1 of the supplementary information. The intensity of the primary (200) reflection for NiO at 43.3 °2Θ increases with increasing Ni weight loading for the series of Ni/ZnO catalysts. Compared to Ni/SiO$_2$, Ni/ZnO displays NiO (200) reflections that are shifted to lower angles, indicating an expansion in lattice parameter and inclusion of Zn$^{II}$ into the crystal lattice. Lattice parameters determined from Rietveld Refinement of the XRD data are shown in Table 3-1. The extent of Zn$^{II}$ substitution in the NiO lattice can be calculated from the NiO lattice parameter using the known lattice parameters of pure NiO (4.178 Å) and Ni$_{0.7}$Zn$_{0.3}$O (4.211 Å) and a linear relationship between Zn content and lattice parameter, as demonstrated by Gaskell et al.$^{59,60}$ The Zn content ranges from 15 – 18 % in the Ni/ZnO catalysts, well below the solubility limit of 32 % in bulk NiO.$^{59}$ The insensitivity of Zn content with Ni loading is a result of having an infinite source of ZnO, leading to a similar crystal structure for NiO in each case. Crystallite sizes for NiO and ZnO were determined using the Scherrer formula and are displayed in Table 3-1. As expected, the NiO crystallite size increases with weight loading, from 18 nm (1 wt. %) to 31 nm (10 wt. %). Interestingly, the ZnO crystallite size also increases monotonically with Ni loading, suggesting Ni facilitates the growth of ZnO. We hypothesize that as the concentration of Ni increases, the propensity for Zn$^{II}$ diffusion also increases due to its ability to substitute for Ni$^{II}$ in the crystal lattice of adjacent NiO NPs. An increased propensity for Zn$^{II}$ diffusion would explain the
observed ZnO size increase with Ni loading. BET surface areas (Table 3-1) also decrease monotonically with Ni loading, consistent with the analysis of crystallite size.

Low magnification TEM of 2 wt. % Ni/ZnO after calcination at 450 °C (Figure 3-2A) shows the polydisperse particle sizes of ZnO ranging from ~10 to ~100 nm. Differentiation between NiO and ZnO in TEM based on contrast alone proves difficult due to the similar atomic numbers of Ni (28) and Zn (30). Figure 3-2B is a representative HRTEM image of the sample, with the fast Fourier transforms (FFTs) of a ZnO particle and NiO particle shown in Figure 3-2C and Figure 3-2D, respectively. The zone axes of the ZnO and NiO particles are [121] and [011], respectively. No species other than ZnO and NiO were observed in the HRTEM images. Electron energy-loss spectroscopy (EELS) was also performed in STEM mode and concentration maps of Ni and Zn were calculated from integration of the Ni and Zn edges, respectively. Representative elemental maps are shown in Figures S3-2A and S3-2B of the supplementary information. The elemental maps illustrate the doping of Zn\textsuperscript{II} in the NiO NPs, supporting the results from XRD. Line scans across the NiO NPs show that Zn\textsuperscript{II} is evenly distributed throughout the NiO particles.
Figure 3-1. Powder X-ray diffraction of Ni/SiO$_2$ and Ni/ZnO catalysts after calcination at 450 °C. The weight loadings of the Ni/ZnO catalysts (0.5, 1, 2, 5, or 10 wt. %) are indicated next to each diffractogram. The dotted line indicates the position of the (200) reflection for pure NiO. Complete PXRD patterns are shown in Figure S3-1 of the supplementary information.
Table 3-1. Results from powder X-ray diffraction of catalysts after calcination.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt. % Ni</th>
<th>NiO a(Å)(^a)</th>
<th>% Zn in NiO(^b)</th>
<th>Crystallite Size (nm)(^c) NiO</th>
<th>Crystallite Size (nm)(^c) ZnO</th>
<th>BET Surface Area (m(^2)/g)</th>
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</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>14</td>
</tr>
<tr>
<td>Ni/ZnO</td>
<td>0.5</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.194 ± 0.001</td>
<td>15 ± 2</td>
<td>21</td>
<td>28</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.194 ± 0.001</td>
<td>15 ± 2</td>
<td>26</td>
<td>39</td>
<td>15.9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>4.195 ± 0.001</td>
<td>16 ± 2</td>
<td>31</td>
<td>56</td>
<td>13.3</td>
</tr>
<tr>
<td>Ni/SiO(_2)</td>
<td>2</td>
<td>4.174 ± 0.001</td>
<td>--</td>
<td>20</td>
<td>--</td>
<td>278</td>
</tr>
</tbody>
</table>

\(^a\)Determined from Rietveld Refinement of the complete powder XRD data.

\(^b\)Calculated from the NiO lattice parameter based on lattice parameters of pure NiO (4.178 Å) and Ni\(_{0.7}\)Zn\(_{0.3}\)O (4.211 Å) and a linear relationship between Zn content and lattice parameter.\(^{59,60}\)

\(^c\)Calculated from FWHM of primary reflection using the Scherrer equation.

\(^d\)Not determined due to the low concentration of Ni in the sample.
Figure 3-2. (A) Low magnification transmission electron microscopy image, (B) HRTEM image, and corresponding FFT of (C) ZnO support and (D) NiO nanoparticle of 2 wt. % Ni/ZnO after calcination at 450 °C. The ZnO particle is viewed from the [12̅1] zone axis, while the NiO particle is viewed from the [01̅1] zone axis.
### 3.4.2. In situ X-ray absorption spectroscopy

Structural changes during the reduction of Ni/ZnO were monitored by in situ X-ray absorption spectroscopy (XAS) during temperature-programmed reduction (TPR). Figure 3-3 shows the evolution of the Ni K-edge XANES of 2 wt. % Ni/ZnO from 200 to 650 °C. The spectra from 200 - 300 °C are consistent with NiO. Upon reaching a temperature of 350 °C, there is a decrease in the height of the white line peak which corresponds to the transition from Ni$^{II}$ to Ni$^{0}$. Correspondingly, there is a shift in the onset of absorption (edge position) to lower energies which is also consistent with the reduction of NiO.
Figure 3-3. Ni K-edge XANES showing the temperature evolution of the in situ reduction of 2 wt. % Ni/ZnO at a ramp rate of 1.3 °C/min and a 50 mL/min flow of 5% H₂/He. Ni is reduced from Ni⁺⁺ to Ni⁰ at ~350 °C as evidenced by a decrease in the height of the edge and a shift in energy of the onset of absorption.
To determine the number of species present during reduction, it is helpful to examine the XANES scans overlaid in a 2-dimensional image (Figure 3-4A). In this figure, there is no clear set of isosbestic points (the points at which all scans intersect). However, the XANES scans recorded from 102 - 507 °C (Figure 3-4B) display a series of isosbestic points. Spectra recorded at temperatures greater than 507 °C (Figure 3-4C) do not intersect the isosbestic points in Figure 3-4B; instead, these spectra exhibit a new set of isosbestic points. Figure 3-4B demonstrates that only two primary species are present up to ~500 °C. The spectrum recorded at 102 °C is identical to NiO; thus one of the primary species is NiO. The other primary species may be identified as α-NiZn, a Ni-rich substitutional solid solution with an FCC unit cell. The spectrum for the Ni$_4$Zn (α-NiZn) reference compound is plotted in Figure 3-4B along with the in situ data. Ni$_4$Zn intersects at each of the isosbestic points formed by the data. Thus, it is clear that there is a direct transition from NiO to α-NiZn with a Zn concentration near 20 mol % (that of Ni$_4$Zn). In addition to Ni$_4$Zn, the spectra in Figure 3-4B were overlaid with the spectra for pure Ni foil, intermetallic β$_1$-NiZn, and intermetallic Ni$_5$Zn$_{21}$ (shown in Figure 3-4D), but these spectra do not intersect the isosbestic points. This set of XANES reference materials encompasses all of the known Ni-Zn phases that form below 700° C and have Zn contents less than 90 %. It is likely that α-NiZn forms at the interface of the NiO and ZnO as the reduction takes place. The spectra recorded from 525 to 636 °C demonstrate that a second phase change takes place (Figure 3-4C). These data show two isosbestic points that are different from the scans from 102 - 507 °C and intersect with the intermetallic β$_1$-NiZn reference spectrum. Thus, the Ni phase undergoes a second transition from α-NiZn to β$_1$-NiZn starting at ~525 °C. We rule out the possibility of formation of the high temperature cubic β-NiZn phase since the temperature required for formation is ~700 °C based on the published Ni-Zn bulk phase diagram. The spectrum for Ni$_5$Zn$_{21}$ was also compared with the data in Figure 3-4C, and it does not intersect at the isosbestic points. The analysis of the isosbestic points of the temperature dependent XANES data shows that three primary Ni-based
phases are present, with NiO transforming first to $\alpha$-NiZn followed by a transformation to $\beta_1$-NiZn.

We performed principal component analysis (PCA) of the XANES data following the methods of Wang et al.\textsuperscript{37} to provide another measure of the number of phases present in the XANES data. The XANES spectra $\mu(E)$ in the energy range of 8307 to 8399 eV and temperature range of 102 to 636 °C were used for calculation of the eigenvectors of the data set. Subsequently, the data were fit with a linear combination of the two principal components (Figure 3-5A). The data and the two-component fit display a significant misfit in the region of 8350 – 8360 eV, indicating two principal components do not adequately reproduce the data. The fit residuals (Figure 3-5B) show peaks at 470 and 630 °C which are consistent with phase transformations at these temperatures. Using three principal components to reproduce the data (Figure 3-5C) results in an improved fit and residuals (Figure 3-5D) within the statistical noise in the data.
Figure 3-4. (A) Normalized Ni K-edge XANES spectra for the temperature-programmed reduction of 2 wt. % Ni/ZnO at a ramp rate of 1.3 °C/min under a 50 mL/min flow of 5 % H₂/He; (B) subset of XANES spectra from 102 – 507 °C shown along with the Ni₄Zn reference spectrum; (C) subset of XANES spectra from 525 – 636 °C shown along with the NiZn reference spectrum; (D) reference XANES spectra for Ni foil, bulk Ni₄Zn, bulk NiZn, bulk Ni₅Zn₂₁, and NiO. In (B) and (C), asterisks indicate the position of isosbestic points.
Figure 3-5. Principal component analysis of the Ni K-edge XANES spectra for the temperature-programmed reduction of 2 wt. % Ni/ZnO at a ramp rate of 1.3 °C/min under a 50 mL/min flow of 5 % H₂/He. (A) representative spectrum (dots) superimposed with the linear combination fitting of two principal components (solid line); (B) residual plot produced from the two-component fit to the data; (C) representative spectrum (dots) superimposed with the linear combination fitting of three principal components (solid line); (D) residual plot produced from the three-component fit to the data.
Principal component analysis and the analysis of isosbestic points are both consistent with three phases present during the in situ reduction: NiO, α-NiZn, and β_1-NiZn. We used linear combination fitting of the XANES spectra to determine the percentage of each phase present during reduction. Since the data has been collected at different temperatures, it is inappropriate to use the room temperature reference spectra in Figure 3-4D for linear combination fitting. Instead, we used IKSFA^{56} to determine which of the XANES spectra were most fundamental (i.e. the spectra that best represent the entire data set through a linear combination of these spectra), and fit the rest of the data with a linear combination of these spectra. IKSFA resulted in an intermediate component at a temperature of 507 °C, which we assign to α-NiZn. The XANES data were then fit with a linear combination of the first spectrum, the spectrum at 507 °C, and the last spectrum to give the results shown in Figure 3-6. Since IKSFA was used to determine the XANES spectra used for linear combination fitting (and no true temperature-dependent reference materials were used), the mole fractions of α-NiZn and β_1-NiZn are, by definition, 1 at 507 and 636 °C, respectively. However, this is an artifact of the data analysis procedure and the sample may actually be composed of multiple phases at 507 and 636 °C. Additionally, the transitions are probably smoother, as the abrupt changes from one composition to another may also be a result of the data analysis procedure. However, Figure 3-6 still provides a qualitative assessment of the stepwise transformation of NiO to α-NiZn and finally β_1-NiZn.
Figure 3-6. Phase composition of each XANES spectra during the temperature-programmed reduction of 2 wt. % Ni/ZnO as determined from factor analysis using a three-component fit.
The temperature evolution of the Fourier transform R-space EXAFS is shown in Figure 3-7. No phase corrections in the EXAFS data have been performed. The peak at low temperatures at 1.6 Å corresponds to contributions from the nearest oxygen neighbor of NiO. The low temperature peak at 2.5 Å corresponds to contributions from the nearest Ni atom in NiO. As the reduction proceeds, these two primary peaks disappear and are replaced by a single peak centered at 2.2 Å, characteristic of Ni or Zn nearest neighbors. The EXAFS results are consistent with the results of XANES. Quantitative analysis of the EXAFS was not performed due to the increase in EXAFS Debye-Waller factor at high temperatures, which significantly reduces the magnitude of EXAFS oscillations and makes differentiation between structures difficult. Additionally, differentiation between Ni and Zn backscatterers proves difficult because they have similar EXAFS phase shifts and backscattering amplitudes as a result of being separated by only one element on the periodic table.
Figure 3-7. Fourier transform Ni K-edge R-space EXAFS spectra of the in situ reduction of 2 wt. % Ni/ZnO. Labels indicate the presence of two peaks which represent Ni-O and Ni-Ni scattering of NiO at low temperatures and a single peak characteristic of Ni-M (M = Ni or Zn) scattering at high temperatures.
3.4.3. Temperature programmed reduction

Figure 3-8 shows the hydrogen consumption during the temperature programmed reduction (TPR) of the 2 wt. % Ni/ZnO catalyst. The temperature ramp rate for this experiment is 10 °C/min compared to the 1.3 °C/min ramp rate of the in situ XAS experiment. The data exhibit two peaks centered at 400 and 550 °C, respectively. The data were fit with two Gaussian-shaped peaks which we attribute to the reduction of two different species. Based on the results obtained from the XANES data, we assign the 400 °C peak to the reduction of NiO since this temperature is consistent with the temperature at which NiO transformed to α-NiZn (as shown in Figure 3-6). Also based on the results shown in Figure 3-6, the only reducible species present above 500 °C is ZnO. Therefore, we assign the second peak centered at 550 °C to the reduction of ZnO. The moles of hydrogen consumed in the first and second peaks are 1.08 and 0.97 eq of Ni in the sample, respectively. These results suggest that equal amounts of NiO and ZnO are reduced which is consistent with the stoichiometry necessary for the formation of intermetallic NiZn.
Figure 3-8. Ex situ temperature-programmed reduction of 2 wt. % Ni/ZnO (10 °C/min, 50 mL/min 3.88 % H₂/Ar). Data (solid black) was fit (dotted green) with two Gaussian-shaped peaks (dotted blue and dotted red). The first and second peaks are assigned to the reduction of Ni (1.08 eq Ni) and Zn (0.97 eq Ni), respectively.
3.4.4. Ex situ characterization of Ni/ZnO after reduction

A low magnification TEM image of the 2 wt. % Ni/ZnO catalyst after reduction is presented in Figure 3-9A. Contrary to the TEM images after calcination, the metallic nanoparticles now show contrast with respect to the ZnO support. In Figures 3-9B-D, HRTEM images of metallic nanoparticles adsorbed to the ZnO support are shown. FFTs of the metallic nanoparticles (boxed areas) are shown in the inset of each HRTEM image. By comparing the experimental distances and angles of the vectors in the FFT to those of possible structures including ZnO, Ni, α-NiZn, β1-NiZn, and NiO, the FFT in Figure 3-9B was indexed to the [100] zone axis of β1-NiZn. The vector lengths of and the angle between the (011) and (011) vectors are 2.03 Å and 77.5°, respectively. This is compared to the expected vector lengths and angle for β1-NiZn (a = 2.751 Å, c = 3.181 Å) of 2.08 Å and 81.7°, respectively. A calculated FFT of a distorted β1-NiZn unit cell with a small elongation in the c direction and compression in a and b directions, with lattice parameters a = 2.61 Å and c = 3.24 Å, matches the experimental FFT shown in Figure 3-9B. The FFT in Figure 3-9C can also be indexed to β1-NiZn, where this particle is oriented along the [111] zone axis. The vector lengths of and angle between the (101) and (011) vectors are 2.03 Å and 66°, respectively, compared to the expected vector lengths and angle for β1-NiZn of 2.08 Å and 65°, respectively. Similar to the structure of the particle in Figure 3-9B, the structure of the particle in Figure 3-9C matches more closely to a distorted β1-NiZn unit cell. The vector lengths of and angle between the (011) and (011) vectors of the particle in Figure 3-9D (2.04 Å and 96°, respectively) also have slight deviations compared to those of the β1-NiZn (2.08 Å and 98°, respectively) and would match a distorted β1-NiZn unit cell.

The three examples of β1-NiZn shown in Figure 3-9 demonstrate the presence of β1-NiZn, but they neither prove that the entire catalyst is homogenous nor do they disprove the presence of other Ni-Zn phases such as α-NiZn. However, the HRTEM results do provide a qualitative assessment of the composition of the Ni-Zn NPs and they support the results from the in situ
XANES experiments. A portion of the Ni-Zn NPs appeared to be encased in an amorphous oxide shell, with an example shown in Figure 3-9C. Other NPs, such as the particle shown in Figure 3-9D, show lattice planes that extend to the surface. It is possible that the oxide shell formed during a short (~ 1 min) exposure of the sample to air during loading into the TEM.
Figure 3-9. Transmission electron microscopy images of 2 wt. Ni/ZnO reduced at 600 °C. (A) Low magnification TEM image, (B-D) HRTEM images of $\beta_1$-NiZn nanoparticles. Insets show indexed FFTs of boxed areas. The $\beta_1$-NiZn particles are viewed from the [100], [111], and [100], zone axes in images (B), (C), and (D), respectively.
The results of ex situ XRD after reduction are shown in Figure 3-10 and Table 3-2 with the complete patterns shown in Figure 3-S3 of the supplementary information. In addition to 2 wt. % Ni/ZnO, we also examined 0.5, 1.0, 5.0, and 10 wt. % Ni/ZnO catalysts. After reduction (3.88 % H₂ in Ar, 10 °C/min to 600 °C), each of the catalysts display a primary reflection that has shifted to lower angles and is characteristic of a larger unit cell and thus a Ni-Zn structure. The shift to lower angles is more pronounced in the low weight loading samples (0.5, 1, and 2 wt. %) than the high weight loading samples (5 and 10 wt. %). This effect can be rationalized in terms of the barrier for Zn\(^{\text{II}}\) reduction and subsequent diffusion into the Ni NPs. The high weight loading samples contain larger Ni crystallites, and correspondingly, low surface-area-to-volume ratios that inhibit Zn incorporation. A quantitative analysis of the ex situ XRD data is not presented because of the inability of these data to describe the physical states of the catalysts under reduction or reaction conditions. The Ni/ZnO peaks can be assigned to the (111) reflection of a face-centered cubic \(\alpha\)-NiZn alloy with an expanded lattice parameter compared to pure Ni metal (e.g. Ni\(_4\)Zn). However, since the catalysts were exposed to air prior to the ex situ XRD analysis, it is likely that the observed reflection for \(\alpha\)-NiZn is a product of \(\beta_1\)-NiZn decomposition. This decomposition behavior of \(\beta_1\)-NiZn to \(\alpha\)-NiZn and ZnO has previously been demonstrated in the literature by Friedrich et al.\(^{44}\)
Figure 3-10. Ex situ powder X-ray diffraction of Ni/SiO$_2$ and Ni/ZnO catalysts after reduction to 600 °C. The dotted lines indicate the reflections for NiO (200), $\beta_1$-NiZn (101), Ni$_4$Zn (111), and Ni (111).
Table 3-2. Results from ex-situ powder X-ray diffraction of catalysts after temperature-programmed reduction to 600 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt. % Ni</th>
<th>Position of Primary Reflection (°2Θ)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>0</td>
<td>--</td>
<td>20</td>
</tr>
<tr>
<td>Ni/ZnO</td>
<td>0.5</td>
<td>d</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>43.82</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>43.85</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>43.97</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>44.24</td>
<td>23</td>
</tr>
<tr>
<td>Ni/SiO2</td>
<td>2</td>
<td>--</td>
<td>20</td>
</tr>
</tbody>
</table>

*Calculated from FWHM of primary reflection using the Scherrer equation.

*Not determined due to the low concentration of Ni in the sample.
In addition to laboratory XRD, we employed synchrotron XRD and pair distribution function (PDF) analysis of the catalysts. The radial distribution functions \( G(r) \) are shown in Figure S3-4 of the supplementary information. Since the radial distribution functions are not elemental specific, the ZnO was fitted and subtracted from each spectrum to gain insight into the nature of the Ni phase. The results from fitting the NiO phase in each of the calcined samples are shown in Table S3-1. The data provided similar results to the laboratory XRD analysis.

3.4.5. Selectivity for acetylene semi-hydrogenation in the presence of ethylene

The selectivity for acetylene semi-hydrogenation in the presence of excess ethylene was measured in a batch reactor following the method we previously used.\(^{29}\) The catalytic behavior of 2 wt. % Ni/ZnO was examined after three different reduction temperatures (400, 500, and 600 °C) and compared with 2 wt. % Ni/SiO\(_2\) reduced at 450 °C. The reactions were carried out at a temperature of 160 °C with a reactant mixture consisting of 5 Torr \(^{13}\)C\(_2\)H\(_2\), 26 Torr H\(_2\), and 53 Torr \(^{12}\)C\(_2\)H\(_4\). Isotopic labeling allows for the direct determination of ethylene selectivity.\(^{29}\)

The partial pressures of \(^{13}\)C\(_2\)H\(_2\), \(^{13}\)C\(_2\)H\(_4\), \(^{13}\)C\(_2\)H\(_6\), and \(^{12}\)C\(_2\)H\(_6\) as a function of time are shown in Figure 3-11. Time 0 is defined as the time at which the reactor reached 160 °C. The reactor took ~10 min to heat from room temperature to 160 °C; thus, there is an inherent offset in the x-axis time values due to the inability to heat the reactor instantaneously. The 2 wt. % Ni/ZnO catalyst reduced at 600 °C (Figure 3-11A) has a low propensity for over-hydrogenation, producing very little \(^{13}\)C\(_2\)H\(_6\) and \(^{12}\)C\(_2\)H\(_6\). Additionally, the same catalyst produces 0.9 Torr \(^{13}\)C\(_2\)H\(_4\) at full conversion of acetylene, which had a starting pressure of 5.3 Torr, which amounts to only 17 % conversion of the acetylene to ethylene. Ni/SiO\(_2\) (Figure 3-11B), conversely, converts 40 % of the starting acetylene to ethylene and produces substantial amounts of \(^{12}\)C\(_2\)H\(_6\) after all of the acetylene has reacted. 2 wt. % Ni/ZnO reduced at 400 and 500 °C showed similar catalytic behavior to the 600 °C reduction temperature, with the results shown in Table 3-3 (time
dependent behavior for these materials is shown in Figure S3-5 of the supplementary information). The reduction temperature of Ni/ZnO (400, 500, or 600 °C) does not appear to be critical to selectivity. Compared to Ni/SiO$_2$, Ni/ZnO exhibits a reduction in turnover frequency and a significant reduction in ethylene formation. The reduction in ethylene formation is a result of an increase in oligomerization on the ZnO-supported catalysts. In fact, all of the Ni/ZnO catalysts convert ~80% of the initial acetylene to oligomers, based on a carbon balance.

Pure ZnO recorded a measurable conversion of acetylene (Figure S3-5 of the supplementary information), oligomerizing acetylene to form 99% higher molecular weight products, with only 1% of the acetylene converted to ethylene. The rate of acetylene removal was 2 – 5 times slower (on a per gram basis) than that of the Ni/ZnO catalysts. Thus, it is clear that it is important to consider the effect of ZnO when evaluating the selectivity of Ni/ZnO catalysts. However, since ZnO converts acetylene to oligomers (instead of hydrogenation products), it is imperative that an absolute measure of ethylene selectivity is used for evaluation. Conversely, previous studies$^{28,31}$ have measured ethane concentration alone as a measure of ethylene selectivity, where catalysts that produced low concentrations of ethane were regarded as selective catalysts. However, by this definition, ZnO would be considered a selective catalyst, when in reality it produces very little ethylene.
Figure 3-11. Partial pressures of $^{13}\text{C}_2\text{H}_2$ (black), $^{13}\text{C}_2\text{H}_4$ (blue), $^{12}\text{C}_2\text{H}_6$ (red), and $^{13}\text{C}_2\text{H}_6$ (green) as a function of time during the catalytic hydrogenation of acetylene in the presence of ethylene in a batch reactor at 160 °C for (A) 200 mg 2 wt. % Ni/ZnO reduced at 600 °C and (B) 15 mg 2 wt. % Ni/SiO$_2$ reduced at 450 °C. Initial partial pressures of $^{13}\text{C}_2\text{H}_2$, $\text{H}_2$, and $^{12}\text{C}_2\text{H}_4$ were ~5 Torr, 26 Torr, and 53 Torr, respectively. The solid line indicates the time at which the reactor reached 160 °C.
Table 3-3. Catalytic activity and selectivity for the semi-hydrogenation of acetylene in the presence of ethylene in a batch reactor at 160 °C. Initial partial pressures of $^{13}$C$_2$H$_2$, H$_2$, and $^{12}$C$_2$H$_4$ were ~5 Torr, 26 Torr, and 53 Torr, respectively.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reduction Temperature (°C)</th>
<th>Rate ($\frac{\text{mol} C_2H_2}{\text{g cat} \cdot \text{s}}$)</th>
<th>TOF (s$^{-1}$)</th>
<th>$^{13}$C$_2$H$_4$ Selectivity$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/SiO$_2$</td>
<td>450</td>
<td>$5.9 \times 10^{-7}$</td>
<td>$3.5 \times 10^{-2}$</td>
<td>40</td>
</tr>
<tr>
<td>Ni/ZnO</td>
<td>400</td>
<td>$8.9 \times 10^{-9}$</td>
<td>$5.5 \times 10^{-4}$</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>$2.5 \times 10^{-8}$</td>
<td>$1.6 \times 10^{-3}$</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>$2.1 \times 10^{-8}$</td>
<td>$1.3 \times 10^{-3}$</td>
<td>17</td>
</tr>
<tr>
<td>ZnO</td>
<td>500</td>
<td>$5.2 \times 10^{-9}$</td>
<td>$6.3 \times 10^{-6}$</td>
<td>1</td>
</tr>
</tbody>
</table>

$^{13}$C$_2$H$_4$ selectivity is defined as the final partial pressure of $^{13}$C$_2$H$_4$ divided by the initial partial pressure of $^{12}$C$_2$H$_2$. 

To gain additional insight into the catalytic behavior of the catalysts, we measured the rate of H-D exchange on Ni/SiO$_2$, Ni/ZnO reduced at 500 °C, and ZnO. The temperature dependence of the H-D exchange is shown in Figure 3-12. Ni/SiO$_2$ has the highest rate of H-D exchange, reaching near HD equilibrium at ~100 °C. For Ni/ZnO and ZnO, temperatures of 150 °C and 200 °C, respectively, are required for similar levels of HD formation.
Figure 3-12. Temperature dependence of H-D exchange with equal H$_2$ and D$_2$ flow rates (10 mL/min).
3.5. Discussion

Our results demonstrate that the calcination of nickel nitrate on a ZnO nanoparticle support leads to Zn-doped NiO NPs with a formula of ca. Ni$_{0.84}$Zn$_{0.16}$O and the rock salt crystal structure. The XANES analysis of the in situ reduction shows a direct transition from the Zn-doped NiO NPs to Ni$_x$Zn$_{1-x}$, a Ni-rich substitutional solid solution with the face centered cubic structure. Thus, it is reasonable for us to conclude that the Zn present in the Ni NPs during the initial phases of the reduction was incorporated during the calcination step. At ~550 °C, Ni$_x$Zn$_{1-x}$ transformed to intermetallic $\beta_1$-NiZn, with the fraction of $\beta_1$-NiZn in the sample increasing with temperature. Contrary to the initial stages of reduction, the reduction of ZnO and diffusion of Zn at high temperatures is necessary for the increased molar ratio of Zn in the NPs and the formation of intermetallic NiZn. These results are summarized in Scheme 1.
Scheme 3-1. Schematic demonstrating progression of the Ni phases during reduction.
It is important to note that the NiZn phases are not stable when exposed to air. Ex situ XANES spectra at the Ni K-edge of reduced 2 wt. % Ni/ZnO after exposure to air (not shown) demonstrated an increase in the white line height, indicative of the oxidation of Ni. The oxidation of Zn after exposure to air could not be probed by XANES due to the excess ZnO in the sample. However, it has been shown previously that ZnO is a decomposition product of intermetallic NiZn after exposure to oxidizing conditions.\(^4\) In addition, we found no evidence for the formation of Ni-Zn compounds with higher Zn content such as Ni$_5$Zn$_{21}$, presumably due to the high vapor pressure of Zn at the temperatures required to reduce a sufficient amount of Zn to form Ni$_5$Zn$_{21}$.

In our previous work, we examined the selectivity for acetylene semi-hydrogenation on bulk intermetallic Ni-Zn catalysts.\(^2\)\(^9\) We found that a favorable increase in ethylene selectivity could be attributed to a reduced binding energy of acetylene on the catalyst surface due to the incorporation of Zn into the crystal lattice. The reduced binding energy of acetylene combined with only a moderate change in H binding energy led to a reduced propensity for acetylene oligomerization and an increase in ethylene production. In this work, we find that the Ni/ZnO catalysts display a lower selectivity to ethylene production than Ni/SiO$_2$, which is in contrast to the aforementioned bulk intermetallic Ni-Zn catalysts which showed increasing ethylene selectivity with increasing Zn content.\(^2\)\(^9\) Thus, from the results of our current study and from comparison with our previous study, it is clear that the ZnO support has a negative influence on ethylene selectivity. The benefit that β$_1$-NiZn provides in terms of ethylene selectivity is not sufficient to overcome the decrease in ethylene selectivity as a result of acetylene oligomerization on the ZnO support. The observed ethylene selectivities for the Ni/ZnO catalysts (17-20 %) can be thought of as a linear combination of the intrinsic selectivities of β$_1$-NiZn and ZnO, with ZnO dominating acetylene removal. The similarity in catalytic selectivity of the three Ni/ZnO catalysts reduced at 400, 500, or 600 °C further substantiates the conclusion that ZnO is dominating the acetylene removal process. The XANES results show that the incorporation of Zn into the Ni
phase increases with increasing temperature, while the catalytic selectivity results provide no indication that additional Zn content favors ethylene selectivity.

The H-D exchange experiments provide additional insight into the reason for the catalytic behavior of the Ni/ZnO materials. The ability of Ni/ZnO to dissociate hydrogen is severely reduced compared to Ni/SiO$_2$, with Ni/ZnO not reaching H-D equilibrium until nearly 50 °C higher than Ni/SiO$_2$. Conversely, the calculated adsorption energies of H on Ni (111) and β$_1$-NiZn (101) are 0.46 eV, and 0.47 eV, respectively. Therefore, the difference in the abilities of Ni/ZnO to dissociate hydrogen compared to Ni/SiO$_2$ can be attributed to the presence of ZnO. The presence of ZnO leads to an inability of the catalyst to dissociate hydrogen, thereby favoring acetylene oligomerization over acetylene hydrogenation.
3.6. Conclusions

Through a combination of in situ XANES measurements and ex situ TEM, we have monitored the phase transformations that Ni/ZnO catalysts undergo during reduction. Zn-doped NiO NPs are reduced to form a Ni-rich solid solution (α-NiZn) at 400 °C, and are finally converted to intermetallic β1-NiZn at 550 °C. Catalytic measurements show that, independent of reduction temperature, Ni/ZnO is not a selective catalyst for acetylene semi-hydrogenation in the presence of excess ethylene as a result oligomerization occurring on the ZnO support. This work highlights that the extrapolation from DFT or bulk materials to supported catalysts is often broken due to the complexities that arise in real materials. Further studies on bimetallic Ni-based hydrogenation catalysts should strive to create well-defined intermetallic structures supported on inert materials, minimizing undesired reaction pathways such as the oligomerization of acetylene.
3.7. References


Figure S3-1. Ex situ powder X-ray diffraction patterns (from top to bottom) of 2 wt. % Ni/SiO$_2$, 10 wt. % Ni/ZnO, 5 wt. % Ni/ZnO, 2 wt. % Ni/ZnO, 1 wt. % Ni/ZnO, and 0.5 wt. % Ni/ZnO after calcination at 450 °C.
Figure S3-2. HRTEM EELS maps for 2 wt. % Ni/ZnO after calcination showing Ni (A) and Zn (B) along with the corresponding Ni line scan (C) and Zn line scan (D). The red lines in (A) and (B) denote the position of the line scans in (C) and (D).
Figure S3-3. Ex situ powder X-ray diffraction patterns (from top to bottom) of 2 wt. % Ni/SiO$_2$, 10 wt. % Ni/ZnO, 5 wt. % Ni/ZnO, 2 wt. % Ni/ZnO, 1 wt. % Ni/ZnO, and 0.5 wt. % Ni/ZnO after reduction to 600 °C.
Figure S3-4. Representative pair distribution functions (PDF) for 10 wt. % Ni/ZnO. (A) ZnO (red line) was fit and subtracted from the data (blue line) to yield the difference (black line); (B) The difference spectrum obtained from the top chart (blue line) was fit with the face-centered cubic structure of Ni (blue line), which resulted in very little residual (black line).
Table S3-1. Results from ex situ synchrotron XRD and pair distribution function analysis.

<table>
<thead>
<tr>
<th>Wt. % Ni</th>
<th>Pretreatment</th>
<th>NiO a(Å)(^a)</th>
<th>ZnO a(Å)(^b)</th>
<th>ZnO c(Å)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>O(_2)</td>
<td>4.228</td>
<td>3.2501</td>
<td>5.2111</td>
</tr>
<tr>
<td>0.5</td>
<td>O(_2) + H(_2)</td>
<td>3.2507</td>
<td>5.2116</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>O(_2)</td>
<td>4.202</td>
<td>3.2500</td>
<td>5.2119</td>
</tr>
<tr>
<td>1</td>
<td>O(_2) + H(_2)</td>
<td>3.2505</td>
<td>5.2112</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>O(_2)</td>
<td>4.200</td>
<td>3.2499</td>
<td>5.2096</td>
</tr>
<tr>
<td>2</td>
<td>O(_2) + H(_2)</td>
<td>3.2512</td>
<td>5.2115</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>O(_2)</td>
<td>4.195</td>
<td>3.2501</td>
<td>5.2094</td>
</tr>
<tr>
<td>5</td>
<td>O(_2) + H(_2)</td>
<td>3.2514</td>
<td>5.2107</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>O(_2)</td>
<td>4.195</td>
<td>3.2500</td>
<td>5.2086</td>
</tr>
<tr>
<td>10</td>
<td>O(_2) + H(_2)</td>
<td>3.2509</td>
<td>5.2093</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)NiO and Ni lattice parameters determined from fitting the radial distribution function G(r) after subtracting the ZnO support.

\(^b\)Calculated from fitting the radial distribution function G(r).
Figure S3-5. Partial pressures of $^{13}$C$_2$H$_2$ (black), $^{13}$C$_2$H$_4$ (blue), $^{12}$C$_2$H$_6$ (red), and $^{13}$C$_2$H$_6$ (green) as a function of time during the catalytic hydrogenation of acetylene in the presence of ethylene in a batch reactor at 160 °C for (A) 2 wt. % Ni/ZnO reduced at 400 °C, (B) 2 wt. % Ni/ZnO reduced at 500 °C, and (C) ZnO pretreated at 500 °C. Initial partial pressures of $^{13}$C$_2$H$_2$, H$_2$, and $^{12}$C$_2$H$_4$ were ~5 Torr, 26 Torr, and 53 Torr, respectively. The solid line indicates the time at which the reactor reached 160 °C.
Chapter 4

Isolated Catalytic Clusters in the Intermetallic Gamma-Brass Crystal Structure of Group X/II Metals

4.1. Introduction

The isolation of active catalytic atoms in inert matrices can yield highly selective and active catalysts and efficient utilization of noble metals. For example, isolated Pd atoms in Cu alloy surfaces selectively catalyze acetylene and styrene hydrogenation as a result of facile hydrogen dissociation on the isolated sites.\(^1\)\(^2\) Pairs of Pd monomers on Au alloy surfaces demonstrate high selectivity for the acetoxylation of ethylene to vinyl acetate, inhibiting the formation of undesirable by-products.\(^3\)

A unique subset of isolated catalysts is intermetallic compounds, which, unlike alloy catalysts, possess a determined crystal structure with a homogeneous distribution of active sites. Recent examples of highly-selective intermetallic compounds include Al\(_{13}\)Fe\(_4\),\(^4\) Pd-Ga,\(^5\)\(^6\) and Ni-Zn,\(^7\) which gain selectivity through both site isolation and alteration of the electronic properties of the active sites. Of particular interest is the \(\gamma\)-brass structure (Cu\(_5\)Zn\(_8\) prototype, space group \(I\bar{4}3m\)) because of its ability to isolate d-block transition metal elements that are often used as catalysts. Furthermore, the \(\gamma\)-brass structure is highly prevalent in binary phase diagrams, showing up in the following systems: Ag-Cd, Ag-Zn, Al-Cu, Au-Cd, Au-Zn, Cd-Cu, Cd-Ni, Cd-Pd, Cd-Pt, Cd-Rh, Co-Zn, Cu-Ga, Cu-Sn, Cu-Zn, Fe-Zn, Ir-Zn, Mn-Zn, Ni-Zn, Pd-Zn, Pt-Zn, and Rh-Zn.\(^8\) We are especially interested in the Ni-Zn system due to its potential usefulness as a selective hydrogenation catalyst.\(^7\) The \(\gamma\)-brass structure is referred to as an “electron phase” as its stability is governed by the per-atom valence electron count. The Hume-Rothery principle of valence electrons predicts that the \(\gamma\)-brass structure has a valence electron concentration of 21 per 13 atoms in the unit cell, independent of the elements involved.\(^9\)
The $\gamma$-brass structure contains a total of 52 atoms per unit cell and four non-equivalent sites, which are depicted in Scheme 1. The sites are described in terms of their spatial relation within the unit cell. The sites termed inner tetrahedral (IT) form a tetrahedron at the center of the unit cell. The outer tetrahedral sites (OT) form a larger tetrahedron around the IT sites. The octahedral sites (OH) form an octahedron around both the IT sites and OT sites, and finally the cuboctahedral (CO) sites form a large distorted cuboctahedron with rectangular instead of square faces. The coordination numbers for each site are shown in Table 4-1.
Scheme 4-1. Illustration of the sites in the $\gamma$-brass structure: inner tetrahedral (IT, red); outer tetrahedral (OT, blue); octahedral (OH, green); and cuboctahedral (CO, orange).
Table 4-1. Description of sites in $\gamma$-brass structure.

<table>
<thead>
<tr>
<th>Site</th>
<th># per unit cell</th>
<th>Coordination #</th>
</tr>
</thead>
<tbody>
<tr>
<td>inner tetrahedral (IT)</td>
<td>8</td>
<td>12 ($3\times IT$, $3\times OT$, $3\times OH$, $3\times CO$)</td>
</tr>
<tr>
<td>outer tetrahedral (OT)</td>
<td>8</td>
<td>12 ($3\times IT$, $3\times OH$, $6\times CO$)</td>
</tr>
<tr>
<td>octahedral (OH)</td>
<td>12</td>
<td>13 ($2\times IT$, $2\times OT$, $1\times OH$, $8\times CO$)</td>
</tr>
<tr>
<td>cuboctahedral (CO)</td>
<td>24</td>
<td>11 ($1\times IT$, $3\times OT$, $3\times OH$, $4\times CO$)</td>
</tr>
</tbody>
</table>
The structure of the Ni-Zn γ-brass phase was first investigated by Schramm et al. who determined the lattice parameter versus composition in the range of approximately 15 to 20 atomic percent Ni.\textsuperscript{10} The lattice parameter exhibited a maximum of $a = 8.926$ Å at 17 atomic % Ni, which was unexpected. Since Zn is larger than Ni, it would be expected that the lattice parameter should decrease with increasing Ni content. Johansson et al. used X-ray and neutron diffraction to elucidate the ordering scheme for this structure, determining that Ni occupies the OT site for the basic stoichiometry Ni\textsubscript{8}Zn\textsubscript{44} (15.4 atomic %).\textsuperscript{11} Because Ni is in the OT site, Ni\textsubscript{8}Zn\textsubscript{44} has no Ni-Ni contacts, whereby each Ni atom is coordinated by 12 Zn atoms in an icosahedral geometry. The OT site is the only site in the unit cell that allows the Ni atoms to be completely isolated, making it obvious that Ni-Zn bonds are preferred over Ni-Ni bonds. However, Johansson et al. were unable to determine the site occupancy for excess Ni (greater than 8 Ni atoms per unit cell).\textsuperscript{11} It is the site occupancy of the excess Ni atoms that defines the arrangement of the Ni-Ni bonds that must occur at concentrations greater than 8 Ni atoms per unit cell to accommodate the extra Ni in the structure.

To determine the effect of bulk structure on the surface concentration of these catalysts, we suggest the use of H\textsubscript{2}-D\textsubscript{2} exchange as a probe reaction. Previous work using alloy catalysts has demonstrated that alloy formation gives rise to differences in the activation barrier for H\textsubscript{2}-D\textsubscript{2} exchange.\textsuperscript{12-13} For Pd-Cu alloys, density functional theory (DFT) has revealed that both the adsorption energy and the activation barrier for hydrogen adsorption and reaction are affected by alloy formation and both must be considered in a microkinetic model.\textsuperscript{13}

In this study, we use neutron powder diffraction to determine the site occupancy of Ni atoms in excess of 8 atoms per unit cell by examining the site occupancy of Ni\textsubscript{8}Zn\textsubscript{44}, Ni\textsubscript{9}Zn\textsubscript{43}, and Ni\textsubscript{10}Zn\textsubscript{42} (hereby referred to as Ni8, Ni9, and Ni10). We show that excess Ni atoms occupy the OH site, thus creating Ni-Ni-Ni trimers in Ni9 and Ni10 that are absent in Ni8. We determine the apparent activation barrier for H\textsubscript{2}-D\textsubscript{2} exchange and use DFT to help relate the observed energies with the probable surfaces of the γ-brass structure. We compare the Ni-Zn catalysts to those from...
the Pd-Zn system, which has previously been shown to adopt the same structure that we find here for the Ni-Zn system.\textsuperscript{14}
4.2. Experimental Methods

4.2.1. Synthesis of Ni-Zn Catalysts

Four Ni-Zn samples with the γ-brass structure were synthesized by adding Ni powder (Sigma Aldrich, <150 μm, 99.999%) and Zn granules (Sigma Aldrich, 3 mm diam, 99.99%) to alumina crucibles (LSP Ceramics, 13 mm i.d.) with the following stoichiometries: Ni$_8$Zn$_{44}$, Ni$_9$Zn$_{43}$, and Ni$_{10}$Zn$_{42}$, and Ni$_{11}$Zn$_{41}$. The samples were sealed in quartz crucibles evacuated to 30 mTorr and heated at a rate of 10 °C/min to 700 °C, held for 24 h, and cooled to room temperature at a rate of 1 °C/min. The ingots were ground in a N$_2$ atmosphere using a stainless steel ball mill (SPEX Mixer/Mill, 8001 sample container). 1 mL of 1,1,1,2,2,3,4,5,5,5 decafluoropentane (Vertrel XF, Dupont) per gram of sample was added to the milling container before milling for 2 h. The samples were unloaded from the mill in an air-free (N$_2$) environment and the decafluoropentane was allowed to evaporate at room temperature. The same procedure was followed for the synthesis of Pd$_8$Zn$_{44}$, Pd$_9$Zn$_{43}$, and Pd$_{10}$Zn$_{42}$, and Pd$_{11}$Zn$_{41}$ using Pd powder (Alfa Aesar, 0.25 – 0.55 μm, 99.95%). Prior to neutron diffraction, the Ni$_8$Zn$_{44}$, Ni$_9$Zn$_{43}$, and Ni$_{10}$Zn$_{42}$ powders were resealed in evacuated quartz tubes and annealed at 500 °C for 7 days to relieve strain from the milling process. Ni$_{11}$Zn$_{41}$ was used only for catalysis measurements and was not examined with neutron diffraction.

4.2.2. Neutron Diffraction

Since the similarity in X-ray scattering factors prevents the use of X-ray diffraction for distinguishing between Ni and Zn, powder neutron diffraction was carried out on the intermetallic compounds. Neutron diffraction measurements were performed on POWGEN, a time-of-flight diffractometer, located at the Spallation Neutron Source at Oak Ridge National Laboratory.
Samples were loaded into 6 mm vanadium cans and measurements were made with a central wavelength of 1.066 Å and a Q range of 1.4 to 20.9 Å⁻¹. All measurements were performed at room temperature. Rietveld Refinement was performed using EXPGUI, a graphical interface for the Los Alamos General Structure Analysis System (GSAS).

4.2.3. X-ray Diffraction

Powder X-ray diffraction was performed on a PANalytical Empyrean X-ray diffractometer using Cu Kα (λ=1.5418 Å) radiation. The samples were analyzed in the cavity of a silicon zero-background holder after leveling with a glass slide. The Empyrean is equipped with a PIXcel detector using scanning line mode detection and the incident beam optics were configured with a ¼° antiscatter slit, 10 mm beam mask, ¼° fixed divergence slit, and 0.04 rad soller slits. Diffracted beam optics were configured with 0.04 rad soller slits, a Ni beta-filter, and a ¼° anti-scatter slit. Diffraction patterns were acquired with a 2Θ step size of 0.025° over a range from 20 to 90 °2Θ.

4.2.4. Surface Area Measurements

The BET surface areas of the Ni-Zn and Pd-Zn catalysts were measured on a Micromeritics Gemini V Surface Area and Pore Size Analyzer. The catalysts were analyzed directly after the completion of the H-D exchange reaction. An approximate weight of 150 mg was used for each catalyst. Data points were taken at P/P⁰ values starting from 0.05 up to 0.25 at an interval of 0.025.
4.2.5. H\textsubscript{2}-D\textsubscript{2} Exchange Experiments

The catalytic H\textsubscript{2}-D\textsubscript{2} exchange reaction was carried out in a tubular flow reactor loaded in a temperature controlled furnace. For each experiment, 200 mg of catalyst was loaded into a 10 mm i.d. fritted glass tube. Quartz wool or silanized quartz wool was not used to support the catalysts because of its non-negligible background reactivity. D\textsubscript{2} (99.6% D\textsubscript{2}, 0.4% HD, Cambridge Isotope Laboratories) and H\textsubscript{2} (99.999%, Praxair) were used without further purification. The catalyst was loaded into the reactor tube in a nitrogen-purged glove box (< 1 ppm O\textsubscript{2} and moisture). The tube was fitted on both ends with 3-way valves to ensure the catalyst is sealed from the atmosphere even after bringing it out of the glovebox. The 3-way valves were purged with flowing H\textsubscript{2} (10 mL/min) prior to admission to the catalyst. Reduction was carried out at 250 °C and held at that temperature for 8 hours with hydrogen flowing through the catalyst at 10 ml/min. Prior to cooling to room temperature, the reaction mixture (10 mL/min D\textsubscript{2} and 10 mL/min H\textsubscript{2}) was admitted to the catalyst bed for 20 min. This was done to ensure equal coverage of adsorbed hydrogen and deuterium at the start of the reaction. For the temperature-programmed reaction, the sample was heated to 250 °C at a rate of 1 °C/min. The reaction run was repeated several times for each catalyst to ensure reproducibility. The outlet gas was analyzed by Hiden HR-20 QIC mass spectrometer to determine the amount of HD formed as a function of temperature. Oxygen, nitrogen, water, HDO and D\textsubscript{2}O were also monitored to ensure that no leaks were present in the reactor. The system was calibrated by measuring the response factors for H\textsubscript{2}, D\textsubscript{2}, and H-D at equilibrium conversion over a highly dispersed Pd/SiO\textsubscript{2} catalyst.
4.3. Results and Discussion

4.3.1. Structural Characterization

The powder X-ray diffraction patterns for Ni8, Ni9, and Ni10 after annealing for 7 days at 500 °C are shown in Figure 4-1. All of the observed peaks correspond to predicted reflections of the γ-Brass crystal structure (space group: I43m, Pearson symbol: cI52, Strukturbericht designation: D82). The most intense peaks at 43° 2Θ correspond to the (411) and (330) lattice planes. While the crystal structure of Ni8, Ni9, and Ni10 are the same, the relative intensities of the peaks in the three structures would be expected to be slightly different as a result of the slight differences in site occupancy. However, since the X-ray scattering factors are nearly identical for Ni and Zn (as a result of being separated by only one element on the periodic table), it is impossible to differentiate between the three structures using X-ray diffraction.
Figure 4-1. Powder X-ray diffraction patterns for annealed $\text{Ni}_9\text{Zn}_{44}$, $\text{Ni}_9\text{Zn}_{43}$, and $\text{Ni}_{10}\text{Zn}_{42}$.
Neutron diffraction, on the other hand, makes it possible to differentiate between small differences in site occupancy as a result of the large difference in neutron scattering factors between Ni and Zn. The neutron diffraction patterns for Ni8, Ni9, and Ni10 are shown in Figure 4-2, with the results of the Rietveld Refinement of the data shown in Table 4-2. Rietveld Refinement was used to determine the site occupancy for Ni in excess of 8 atoms per unit cell using the following method: First, the previously established conclusion that the first 8 Ni atoms (i.e. all of the Ni atoms in Ni8) occupy the OT site\textsuperscript{11} was verified by fitting Ni8 with 4 models, one with all 8 Ni atoms on each of the four different sites: IT, OT, OH, and CO. The refinement with the lowest R-factor (and the only one that produced a reasonable fit to the data) was that with Ni atoms on the OT site, thus verifying the previously established results. The Ni atoms are spaced out as much as the structure allows in Ni8, as each Ni atom has exactly 12 Zn near neighbors in an icosahedral geometry. The stacking pattern of these icosahedra is illustrated in Figure 4-3 where each icosahedron shares 6 vertices and 3 faces with neighboring icosahedra.

To determine the site occupancy for the additional Ni atom in Ni9 and the two additional Ni atoms in Ni10, three Rietveld Refinement models were created for each sample: one model for the additional Ni atom(s) on the IT, OH, or CO sites. For both Ni9 and Ni10, the quality of the fit only improved with the additional Ni atom(s) on the OH site. Thus, we can conclude that Ni atoms in excess of 8 per unit cell occupy the OH site. As further evidence, we allowed the site occupation factor (SOF) for Ni on the OH site to vary for the Rietveld Refinement of each of the three samples. These results are shown in Table 4-2 and also illustrated in Figure 4-4. For Ni8, Ni9, and Ni10, the SOF for Ni on the OH site is \(0.00 \pm 0.02\), \(0.14 \pm 0.02\), and \(0.22 \pm 0.02\) respectively. Since the OH site has a degeneracy of 8 atoms, these results suggest that 0, 1.7, and 2.6 Ni atoms occupy the OH site in the Ni8, Ni9, and Ni10 structures respectively, consistent with the expectation based on stoichiometry of 0, 1, and 2 atoms for Ni8, Ni9, and Ni10, respectively. This expectation based on stoichiometry and perfect substitution of additional Ni atoms on the OH site is illustrated with the red line in Figure 4-4.
Figure 4-2. TOF neutron powder diffraction patterns acquired with a central wavelength of 1.066 Å and corresponding Rietveld refinements of Ni$_8$Zn$_{44}$ (a), Ni$_9$Zn$_{43}$ (b), and Ni$_{10}$Zn$_{42}$ (c). The data are shown as black “+” symbols, the fits are shown as continuous red curves, the difference plots are shown below the data as continuous blue curves, and the allowed reflections for the $I4_3m$ space group are indicated by black tick marks.
Table 4-2. Lattice parameters, fractional atomic coordinates, site occupation factors (SOF), isotropic displacement parameters ($U_{iso}$), and fit parameters for Ni$_8$Zn$_{44}$, Ni$_9$Zn$_{43}$, and Ni$_{10}$Zn$_{42}$ as refined by powder neutron diffraction.

<table>
<thead>
<tr>
<th>site</th>
<th>element</th>
<th>parameter</th>
<th>Ni$<em>8$Zn$</em>{44}$</th>
<th>Ni$<em>9$Zn$</em>{43}$</th>
<th>Ni$<em>{10}$Zn$</em>{42}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$a$ (Å)</td>
<td>8.9228 ± 0.0001</td>
<td>8.9259 ± 0.0001</td>
<td>8.9107 ± 0.0001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi^2$</td>
<td>2.90</td>
<td>5.37</td>
<td>2.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R$</td>
<td>0.1768</td>
<td>0.1281</td>
<td>0.1752</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_{variables}$</td>
<td>24</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_{reflections}$</td>
<td>1421</td>
<td>1424</td>
<td>1469</td>
</tr>
<tr>
<td>IT(8)</td>
<td>Zn</td>
<td>$x=y=z=$</td>
<td>0.1051 ± 0.0002</td>
<td>0.1051 ± 0.0001</td>
<td>0.1054 ± 0.0001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SOF</td>
<td>0.90 ± 0.02</td>
<td>1.00 ± 0.02</td>
<td>1.00 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$U_{iso}$</td>
<td>0.0092 ± 0.0005</td>
<td>0.0097 ± 0.0003</td>
<td>0.0097 ± 0.0004</td>
</tr>
<tr>
<td>OT(8)</td>
<td>Ni</td>
<td>$x=y=z=$</td>
<td>-0.1719 ± 0.0001</td>
<td>-0.1719 ± 0.0001</td>
<td>-0.1718 ± 0.0001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SOF</td>
<td>0.91 ± 0.02</td>
<td>0.97 ± 0.01</td>
<td>0.94 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$U_{iso}$</td>
<td>0.0070 ± 0.0003</td>
<td>0.0070 ± 0.0002</td>
<td>0.0069 ± 0.0003</td>
</tr>
<tr>
<td>OH(12)</td>
<td>Zn</td>
<td>$y=z=0$; $x=$</td>
<td>0.3549 ± 0.0002</td>
<td>0.3552 ± 0.0001</td>
<td>0.3561 ± 0.0002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SOF</td>
<td>1.00 ± 0.02</td>
<td>0.86 ± 0.02</td>
<td>0.78 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$U_{iso}$</td>
<td>0.0115 ± 0.0005</td>
<td>0.0110 ± 0.0004</td>
<td>0.0105 ± 0.0005</td>
</tr>
<tr>
<td>OH(12)</td>
<td>Ni</td>
<td>$y=z=0$; $x=$</td>
<td>0.3459 ± 0.0002</td>
<td>0.3552 ± 0.0001</td>
<td>0.3561 ± 0.0002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SOF</td>
<td>0.00 ± 0.02</td>
<td>0.14 ± 0.02</td>
<td>0.22 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$U_{iso}$</td>
<td>0.0115 ± 0.0005</td>
<td>0.0110 ± 0.0004</td>
<td>0.0105 ± 0.0005</td>
</tr>
<tr>
<td>CO(24)</td>
<td>Zn</td>
<td>$x=y=$</td>
<td>0.3071 ± 0.0001</td>
<td>0.3070 ± 0.0001</td>
<td>0.3075 ± 0.0001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SOF</td>
<td>0.0437 ± 0.0001</td>
<td>0.0435 ± 0.0001</td>
<td>0.0424 ± 0.0001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$U_{iso}$</td>
<td>0.0118 ± 0.0003</td>
<td>0.0115 ± 0.0002</td>
<td>0.0123 ± 0.0003</td>
</tr>
</tbody>
</table>
Figure 4-3. Stacking pattern of icosahedrons centered on the OT sites in the structure of Ni$_{10}$Zn$_{44}$. Ni atoms are at the centers and Zn atoms are at the vertices of the icosahedrons. Each icosahedron shares 6 vertices and 3 faces with neighboring icosahedra.
Figure 4-4. Variation in Ni OH site occupation factor with Ni composition for Ni$_8$Zn$_{44}$, Ni$_9$Zn$_{43}$, and Ni$_{10}$Zn$_{42}$. Perfect substitution of additional Ni (greater than 8 Ni atoms per unit cell) on the OH site is modeled by the red line.
The implication of the above results from neutron diffraction is that the Ni atoms in Ni9 and Ni10 are not completely isolated from other Ni atoms. Instead, a portion of the Ni atoms in Ni9 and Ni10 contain bridging Ni atoms to form Ni-Ni-Ni trimers. This is illustrated in Figure 4-5 which shows the \( \gamma \)-brass crystal structure with an exposed (110) face. Figure 4-5A shows only isolated Ni atoms which are present in Ni8, while Figure 4-5B shows a Ni-Ni-Ni trimer that is present in both Ni9 and Ni10. The frequency of Ni-Ni-Ni trimers is equal to the number of Ni atoms in excess of 8 per unit cell. Thus, Ni8, Ni9, and Ni10 have 0, 1, and 2 Ni-Ni-Ni trimers per unit cell, respectively. Using stoichiometry to calculate the number of isolated Ni atoms gives 8, 6, and 4 for Ni8, Ni9, and Ni10, respectively. This is illustrated in Figure 4-6, which shows the number of isolated Ni atoms and the number of Ni-Ni-Ni trimers per unit cell. Ni11 also falls within the compositional limits of the phase and has 3 Ni-Ni-Ni trimers per unit cell. It is apparent from this figure that a small change in Ni concentration gives rise to a large change in the number of Ni trimers and isolated Ni atoms that are present in the structure. Since Ni is active for hydrogen dissociation and Zn is not, it is predicted that Ni9, Ni10, and Ni11 could perform substantially different than Ni8 for a hydrogenation reaction, given the presence of Ni-Ni-Ni trimers.

It has previously been shown using single crystal X-ray diffraction that the site occupancy of the Pd-Zn \( \gamma \)-brass system is identical to what we have described above for Ni-Zn.\(^{14}\) The frequency and arrangement of Pd in Pd8, Pd9, Pd10, and Pd11 remains the equivalent to that of Ni in Ni8, Ni9, Ni10, and Ni11. This congruency between the materials is expected as they are in the same column of the periodic table and have an equivalent number of valence electrons per atom. Therefore, extensive characterization was not carried out on the Pd-Zn materials. Below, we compare the apparent activation barrier for \( \text{H}_2-\text{D}_2 \) exchange on Ni8, Ni9, Ni10, and Ni11 with Pd8, Pd9, Pd10, and Pd11.
Figure 4-5. (a) (110) surface of the $\gamma$-brass crystal structure showing isolated Ni atoms (blue) in a Zn (gray) matrix found in Ni8 and (b) (110) surface of the $\gamma$-brass crystal structure showing the geometry of a Ni-Ni-Ni trimer found in Ni9 and Ni10.
Figure 4-6. Number of isolated Ni atoms and number of Ni-Ni-Ni trimers per unit cell in the Ni-Zn $\gamma$-brass crystal structure.
4.3.2. Catalytic H₂-D₂ Exchange

The catalytic H₂-D₂ exchange reaction is described by the following equation:

\[
H_2 + D_2 \xleftrightarrow{k_{app}} 2 \text{HD}
\]  \hspace{1cm} (1)

where \(k_{app}\) is the apparent rate constant for the forward reaction, \(r_f\). The forward reaction rate is defined in terms of the measured rate of reaction, \(r_{net}\), and the equilibrium constant, \(K_{eq}\):

\[
r_f = \frac{r_{net}}{(1-\eta)}, \text{ where } \eta = \frac{(HD)^2}{[H_2][D_2]K_{eq}} \hspace{1cm} (2)
\]

\(K_{eq}\) is approximated as 4, ignoring the small isotope effect of the reaction.\(^{17}\) Arrhenius plots for the catalytic H₂-D₂ exchange on the Ni-Zn and the Pd-Zn catalysts are presented in Figures 4-7 and 4-8, respectively. The forward rates of reaction were plotted in the Arrhenius plots to eliminate the small effect of approach to equilibrium on data (\(2 \times 10^{-5} < \eta < 0.003\)). The data presented in these figures were acquired at differential conversion, with conversion values ranging from 1% to a maximum of 10%. Two analyses were carried out for each sample with the first represented by red dots and the second by blue. A small amount of deactivation (presumably due to the loss of surface area) accounts for the shifts to lower rates between each reaction run.

The apparent activation barriers determined from the slopes and intercepts of the fits to the data, respectively, are shown in Table 4-3. The BET surface areas, which vary from 0.85 to 1.40 m² g⁻¹, are also shown in Table 4-3.

For the Ni-Zn system, the apparent activation energy for all the four catalysts are effectively same. This suggests that the surface structures of the four catalysts are equivalent, even though the site occupancies of the bulk structures vary. However, in the case of the Pd-Zn
catalysts we notice that Pd$_8$Zn$_{44}$, with a structure that precludes the presence of any Pd trimers, has a significantly higher activation barrier than all the other Pd-Zn catalysts which are expected to have Pd trimers.

The rates at 150 °C were determined by averaging the H-D flow rates over a temperature range of approximately 149.5 °C to 150.5 °C (corresponding to conversions less than 10 %) for each catalyst to minimize any random noise associated with the online measurement system. For the Ni-Zn catalysts, though there is noticeable variation in the TOF values and no particular trend is evident. However, for the Pd-Zn system the TOF value is seen to strictly increase with increasing Pd:Zn ratio. Furthermore, the TOF value for Pd$_8$Zn$_{44}$ is an order of magnitude smaller than the TOF values of all the other Pd-Zn catalysts, but the TOF values of all the Ni-Zn catalysts are of the same order of magnitude.

After the catalytic H$_2$-D$_2$ measurements on the catalysts, diffraction patterns were acquired and are shown in Figures S4-1 and S4-2 for the Ni-Zn and Pd-Zn samples, respectively. No appreciable change in the structures was noticed, with the exception of a small amount of ZnO present in the diffraction patterns. The ZnO is not a result of handling in ambient conditions as this is not present in samples that were not used for catalytic testing. Instead, the ZnO is likely a product of a small oxygen impurity in the gas cylinders reacting with the sample at reaction temperatures to form ZnO.
Figure 4-7. Arrhenius plots for the catalytic H\(_2\)-D\(_2\) exchange on Ni8 (a), Ni9 (b), Ni10 (c), and Ni11 (d) in a plug flow reactor with 10 mL/min H\(_2\) and 10 mL/min D\(_2\) at a conversion of 1 – 10% and a temperature ramp rate of 1 °C/min. Red points indicate data from first analysis and blue points indicate data from second analysis. Black lines are linear fits to the data.
Figure 4-8. Arrhenius plots for the catalytic H$_2$-D$_2$ exchange on Pd8 (a), Pd9 (b), Pd10 (c), and Pd11 (d) in a plug flow reactor with 10 mL/min H$_2$ and 10 mL/min D$_2$ at a conversion of 1–10% and a temperature ramp rate of 1 °C/min. Red points indicate data from first analysis and blue points indicate data from second analysis. Black lines are linear fits to the data.
Table 4-3. Catalytic results for H$_2$-D$_2$ exchange on Ni-Zn and Pd-Zn catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area (m$^2$/g)</th>
<th>$E_{\text{app}}$ (kJ mol$^{-1}$)</th>
<th>Rate @ 150 °C × 10$^7$ (mol m$^{-2}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.79 ± 0.03</td>
<td>82 ± 4</td>
<td>6 ± 1 × 10$^4$</td>
</tr>
<tr>
<td>Ni$<em>8$Zn$</em>{44}$</td>
<td>1.06 ± 0.08</td>
<td>55 ± 2</td>
<td>4 ± 1</td>
</tr>
<tr>
<td>Ni$<em>9$Zn$</em>{43}$</td>
<td>1.38 ± 0.12</td>
<td>53 ± 2</td>
<td>4 ± 1</td>
</tr>
<tr>
<td>Ni$<em>{10}$Zn$</em>{42}$</td>
<td>1.33 ± 0.04</td>
<td>55 ± 2</td>
<td>8 ± 1</td>
</tr>
<tr>
<td>Ni$<em>{11}$Zn$</em>{41}$</td>
<td>1.26 ± 0.09</td>
<td>57 ± 2</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>Pd</td>
<td>0.008 ± 0.001</td>
<td>104 ± 4</td>
<td>1.5 ± 0.1 × 10$^5$</td>
</tr>
<tr>
<td>Pd$<em>8$Zn$</em>{44}$</td>
<td>1.29 ± 0.19</td>
<td>49 ± 2</td>
<td>5 ± 1</td>
</tr>
<tr>
<td>Pd$<em>9$Zn$</em>{43}$</td>
<td>0.85 ± 0.09</td>
<td>42 ± 2</td>
<td>13 ± 1</td>
</tr>
<tr>
<td>Pd$<em>{10}$Zn$</em>{42}$</td>
<td>0.94 ± 0.05</td>
<td>40 ± 2</td>
<td>20 ± 1</td>
</tr>
<tr>
<td>Pd$<em>{11}$Zn$</em>{41}$</td>
<td>1.40 ± 0.05</td>
<td>41 ± 2</td>
<td>22 ± 1</td>
</tr>
</tbody>
</table>
4.4. Conclusions

Using neutron diffraction, we show that Ni atoms in excess of 8 per unit cell in the γ-brass crystal structure occupy the outer tetrahedral (OH) site. This results in Ni-Ni-Ni trimers for the any composition with the general formula Ni$_{8+x}$Zn$_{44-x}$ for $0 \leq x \geq 3$. The generality of the formation of isolated M (M=metal) atoms and M trimers in the M-Zn γ-brass crystal extends past Ni-Zn to many of the other γ-brass systems including those including Pd and Pt. While the bulk structure of the Ni-Zn shows concentration dependence of isolated atoms and trimers, we cannot verify the existence of any difference on the surface from the H$_2$-D$_2$ exchange probe reaction. The results of the Pd-Zn system suggest surface Pd-Pd-Pd trimers in Pd9, Pd10, and Pd11 that are not present in Pd8 decrease the activation barrier for H$_2$-D$_2$ exchange. The usefulness of such catalysts may extend to selective hydrogenation reaction where isolated individual atoms or groups of atoms are beneficial.
4.5. References


(8) Okamoto, H. *ASM International* 2010, 44.


4.6. Supplementary Information

4.6.1. Supplementary Tables and Figures

Figure S4-1. X-ray diffraction patterns for Ni8, Ni9, Ni10, and Ni11 after H₂-D₂ exchange.
Figure S4-2. X-ray diffraction patterns for Pd8, Pd9, Pd10, and Pd11 after H₂-D₂ exchange.
Chapter 5

Illuminating Surface Atoms in Nanoclusters by Differential X-ray Absorption Spectroscopy


The majority of this chapter was written by CSS, however sections 4.2.4 Computational Method and 4.3.2 Atomistic Modeling of Ar-Induced Restructuring were written by TPS. The figures were created by CSS with the exception of Figures 5-5, 5-6, 5-7, 5-8, and S4-4 which were created by TPS.

5.1. Introduction

Nanoscience relies on the ability of researchers to detect ultra-small changes on the atomic scale that arise from the non-bulk-like properties of nanostructures. Applications of such materials are far reaching — extending from drug delivery\(^1\) to catalysis,\(^2\) photonics,\(^3\) magnetic storage,\(^4\) and spintronics.\(^5\) In catalysis, surface atoms of metal nanoparticles (under-coordinated surface atoms in particular) often control catalytic properties.\(^6\)-\(^10\) Detecting the number and coordination environment of surface metal atoms, as well as their response to stimulation (i.e. molecules), is of utmost importance in understanding catalytic behavior. X-ray absorption spectroscopy (XAS) is particularly well-suited for this task due to its sensitivity to local structure (within a few coordination shells around an X-ray absorbing atom) and its ability to be used \textit{in situ}, but the inherent ensemble-averaging nature of XAS measurements that probe both interior and surface types of atoms makes surface characterization difficult. External stimulation, such as the chemisorption of molecules, can be used to enhance the detectability of the surface atoms by XAS. For example, XAS can be used to determine the surface compositions of Pd and Pt in bimetallic nanoparticles by detecting changes in the X-ray absorption near edge structure (XANES) after CO adsorption.\(^11\) The use of differential extended X-ray absorption fine structure (EXAFS) allows for more sensitive detection of local structure compared to traditional EXAFS.
Applied to catalysis, this can isolate the active surface atoms from spectator bulk atoms.$^{12-17}$ Application of this technique to magnetostriction makes detection of femtometer atomic displacements possible.$^{18}$

Despite the number of methods developed in the last decade, improving the selectivity of structural probes to surface metal atoms in nm-scale nanoclusters remains one of the main objectives of catalysis science. In this work we will show the application of a differential EXAFS ($\Delta$-EXAFS) method that we developed for probing surface atoms of SiO$_2$-suppoted Pd nanoclusters. The $\Delta$-EXAFS data were obtained by measuring the EXAFS signals before and after Ar adsorption, and subsequently modeled by taking into account only the unsubtracted (surface) Pd contributions. In addition to the EXAFS data analysis and modeling, we have also employed atomistic molecular dynamics (MD) simulations to differentiate between models compared in the EXAFS data analysis process, thus determining the most plausible restructuring mechanism. Further application of the technique is not limited to a particular set of materials; instead, it can be applied to any system in which modulation causes small changes in local structure.
5.2. Experimental and Computational Methods

5.2.1. Synthesis of Pd/SiO$_2$

A 3% Pd/SiO$_2$ sample was synthesized using the strong electrostatic adsorption (SEA) method, according to a previously reported procedure.$^{19}$ Briefly, Pd(NH$_3$)$_4$(NO$_3$)$_2$ was added to a slurry of silica (Davisil A60) at pH = 11. The sample was filtered, washed, and dried at 398 K prior to reduction at 438 K under flowing 4% H$_2$/He for 1 h.

5.2.2. X-ray Absorption Spectroscopy (XAS)

XAS measurements were performed at beamline 10-BM of the Advanced Photon Source (APS) at Argonne National Lab (ANL). The 3% Pd/SiO$_2$ catalyst (~50 mg) was pressed into a 4 mm ID cylindrical steel holder to obtain an edge step of ~0.4 at the Pd K-edge. The sample was loaded into a specially designed in situ reactor cell (Figure S5-1 in the supplementary information) capable of heating the sample to 523 K for reduction and cooling the sample to 77 K during XAS measurements. After loading the sample, the sample chamber was evacuated to 30 mTorr with a mechanical vacuum pump to ensure all fittings were installed correctly and the system had no leaks. Ultra-high purity (UHP, 99.999%) 3% H$_2$/He was used for pretreatment without further purification. UHP He and UHP Ar were passed through triple gas purifiers to remove oxygen, moisture, and hydrocarbons (Restek Super Clean gas purifier) prior to admission onto the catalyst sample. The sample was purged at room temperature under flowing 3% H$_2$/He at a rate of 30 mL/min for 15 min before heating to 523 K and holding for 1 h. The system was purged with He at a rate of 30 mL/min for 20 min prior to cooling to remove absorbed and adsorbed hydrogen from the Pd nanoclusters (NCs). The sample was then immediately cooled to 77 K by sliding the sample holder into the liquid nitrogen Dewar with a magnet. The temperature
of the catalyst was measured in a separate experiment to be 79 K. However, it is unclear if the
thermocouple was inducing a heat loss and was the cause of the increased temperature. Therefore,
the temperature of the EXAFS measurements will be referred to as 77 K. All EXAFS scans were
acquired in transmission geometry with an energy range from 200 eV before to 1227 eV after the
Pd K-edge (24350 eV). A reference Pd foil was placed between the transmission and reference
ionization chambers for energy calibration and alignment. The EXAFS scans referred to as
“Clean Pd NCs” were acquired under flowing He at a rate of 30 mL/min at 77 K. The EXAFS
scans referred to as “After Ar adsorption” were acquired under a mixture of Ar (5 mL/min) and
He (30 mL/min) at 77 K. At this partial pressure of Ar (~100 Torr), we expect the silica and Pd
surfaces to be covered by approximately one statistical monolayer of Ar based on BET surface
area measurements. The IFEFFIT package was used for XAS data processing, and analysis.20-21
Energy calibration was performed by aligning all scans with the reference Pd foil prior to further
processing. In addition, the parameters used for background normalization were kept constant for
all scans to ensure that no artifacts were generated from the data normalization procedure. To
ensure that the differential EXAFS oscillation produced as a result of subtracting the EXAFS
scans before and after Ar adsorption is not due to a slight shift in the zero-point calibration of the
k-scale, we also reproduced the differential spectrum without alignment of each scan with the
reference Pd foil. Additionally, the data normalization procedure is reproducible across multiple
EXAFS scans.

5.2.3. Scanning Transmission Electron Microscopy (STEM)

STEM images were acquired at the University of Chicago Research Resources Center
facility using a JEOL-ARM 200CF aberration corrected microscope (70 pm spatial resolution and
300 meV energy resolution). STEM imaging for this sample was previously reported.19 Samples
were prepared for analysis by dispersing in isopropyl alcohol, sonicating for 20 min, dropping
onto a holey-copper grid, and drying under a heat lamp for 20 min. Images were taken using the High Angle Annular Dark Field (HAADF) mode and the Particle2 program was used for counting particle sizes. 90 particles were counted to get an accurate representation of the particle size distribution.

### 5.2.4. Computational Method

ReaxFF\textsuperscript{22} is a classical interatomic interaction force-field that consists of both bonding and non-bonding interactions, which enables the potential to describe both metallic bonding and van der Waal interactions that occur in a system consisting of Pd clusters exposed to a noble gas. To treat simulations involving metal/metal and metal/noble gas interactions, we combined a recently developed ReaxFF Pd/Pd\textsuperscript{23} interaction potential (which was trained against DFT and experimental structural data and formation energies for Pd bulk, surfaces, and clusters) with Ar and He parameter sets.\textsuperscript{24} Model 1 nm Pd\textsubscript{13} clusters were generated using a hybrid Monte Carlo-molecular dynamics scheme (MC/MD),\textsuperscript{23} in which MC steps randomly displace Pd atoms in the cluster according to the usual Metropolis criteria.\textsuperscript{25} After every 500 MC trial steps, a 100 ps MD run was conducted to diversify the configuration space explored by the cluster. The temperature of the MC/MD simulation was set to 500 K, which corresponds to the temperature of the experimental system prior to being quenched to 77 K. Hence, the MC/MD simulation yields a set of model clusters in reasonable approximation to those contained in the poly-disperse experimental sample upon exposure to Ar gas.

To assess the impact of an Ar gas phase on Pd cluster reconstruction, we conducted molecular dynamics simulations in the NVT ensemble via the velocity Verlet method\textsuperscript{26} with a 0.25 fs time step. A Berendsen thermostat\textsuperscript{27} with a damping constant of 100 fs was used to maintain a temperature of 77 K through the duration of the 1 ns simulations. The model clusters were equilibrated for 1 ns in vacuum before being exposed to 50 gas phase Ar atoms in a
50×50×50 Å periodic simulation cell (yielding an effective pressure of ~0.5 MPa, estimated from the ideal gas law) for an additional 1 ns. Average Pd-Pd bond distances were determined for each atom from atomic coordinates that were archived at 125 fs intervals throughout the simulation. Additional control simulations were conducted under He to ensure that observed Pd cluster reconstructions can be attributed to the effect of the Ar gas phase.

Nearest-neighbor (NN) coordination numbers were calculated using a cutoff radius of 3.5 Å around each atom. The Ar-induced bond length expansion was calculated by taking the difference between the average NN bond length of each atom before and after being exposed to Ar. The data were averaged over the last 125 ps (1000 frames) of each simulation to obtain representative NN bond lengths and coordination numbers.
5.3. Results

5.3.1. Adsorption of Ar on Pd/SiO$_2$ at 77 K

The Pd K-edge EXAFS data for the Pd nanoclusters (NCs) at 77 K under a He atmosphere (30 mL/min) are shown in Figure 5-1 (referred to as “Clean Pd NCs”). After reducing at a temperature of 523 K with 3% H$_2$/He, the sample was purged with pure He prior to cooling to prevent palladium hydride (PdH$_x$) formation. Based on the Pd-Pd first shell bonding distance, it is clear PdH$_x$ is not present in the sample. The data show only Pd-Pd bonding and there is no indication of low-Z scatterers (e.g. C, O, or N). The first shell was modeled with a single Pd-Pd scattering path and the fit is shown along with the data in Figure 5-1. The results of the fit are shown in Table 5-1. The clean Pd NCs have a Pd-Pd coordination number and bond length of 7.0 ± 0.2 and 2.700 ± 0.005 Å, respectively. The bond length is contracted with respect to Pd foil, indicating the presence of small Pd NCs, which is in agreement with STEM data. The coordination number is consistent with Pd nanoclusters of about 37 atoms (Pt$_{37}$). A Pd$_{37}$ cluster with the hemispherical (111)-truncated cuboctahedron geometry has a first shell coordination number of 6.97 and diameter of 1.1 nm. Attempts to fit the EXAFS data past the first coordination shell following established methods failed due to the high disorder of the ultra-small Pd NCs. A STEM image for the sample is shown in Figure 5-2. The average particle size determined from STEM is 1.0 ± 0.2 nm, which is consistent with the EXAFS results (1.1 nm).
Figure 5-1. (a) Edge-step normalized and background-subtracted $k^2$-weighted $\chi(k)$ EXAFS data and (b) Fourier transform magnitude of $k^2$-weighted $\chi(k)$ for the clean Pd NCs in He atmosphere at 77 K at the Pd K-edge. The first-shell fit of the data is shown in blue.
Table 5-1. Pd K-edge EXAFS first shell fits.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N</th>
<th>r (Å)</th>
<th>( \sigma^2 ) (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd Foil</td>
<td>12</td>
<td>2.731 ± 0.002</td>
<td>0.0058 ± 0.0002</td>
</tr>
<tr>
<td>Clean Pd NCs</td>
<td>7.0 ± 0.2</td>
<td>2.700 ± 0.005</td>
<td>0.0088 ± 0.0002</td>
</tr>
<tr>
<td>After Ar Adsorption</td>
<td>7.2 ± 0.4</td>
<td>2.707 ± 0.008</td>
<td>0.0094 ± 0.0004</td>
</tr>
</tbody>
</table>

*aCalculation of N was performed using the amplitude reduction factor obtained from the Pd foil (0.86).*

*bEXAFS Debye-Waller factor.*
Figure 5-2. (a) STEM image of Pd/SiO$_2$ nanoclusters and (b) particle size distribution of Pd/SiO$_2$ catalyst. The calculated number average particle diameter is $1.0 \pm 0.2$ nm.
After Ar adsorption (5 mL/min Ar in 30 mL/min He), the EXAFS data highly resemble the data for the clean Pd NCs. The first shell fit of the data after Ar adsorption provides identical results (within error) to the clean Pd NCs. This analysis strategy, however, is not adequate for detection of changes that may have occurred in Ar atmosphere because only a few surface atoms of Pd particles would have been affected by Ar while XAS signal probes all atoms in the nanocluster. Differential EXAFS (Δ-EXAFS) spectrum obtained after subtracting the two spectra (the one measured in Ar from the other, measured in He) should have much greater sensitivity to the atoms directly affected by Ar because the contributions to the Δ-EXAFS from unaffected (“spectator”) atoms will cancel. The Δ-EXAFS signal is shown in Figure 5-3. The most striking characteristic of this spectrum is a shift of the phase of the oscillations by ca. π/2, clearly visible in Figure 5-3. We will show analytically below that the π/2 phase shift in the Δ-EXAFS compared to the total spectrum is consistent with the small change of the Pd-Pd bond length provided that the total coordination number of Pd atoms remains approximately the same. After the adsorption of Ar, the sample was heated to room temperature and purged with flowing He (30 mL/min) and subsequently cooled to 77 K. Taking the difference of the clean Pd NCs EXAFS spectrum and a spectrum after heating to room temperature, shows only noise (see Figure S5-2 in the supplementary information): therefore, the observed change in the Pd bond length is reversible. The XANES spectra for the clean Pd NCs, the NCs after after Ar adsorption, and a reference Pd foil are shown in Figure S5-3 in the supplementary information. The XANES of the Pd NCs show little difference before and after Ar adsorption, indicative of no change in electronic structure of the Pd atoms.
Figure 5-3. $k^2$-weighted $\chi(k)$ EXAFS data for the clean Pd NCs, after Ar adsorption, and the $\Delta$-EXAFS spectrum obtained by subtracting the spectrum after Ar adsorption from the clean Pd NCs spectrum. The fit of the $\Delta$-EXAFS data is shown in black. The dotted lines are a guide to the eye to show the $\pi/2$ phase shift of the $\Delta$-EXAFS compared to the original spectrum for Pd NCs. The data are shifted vertically for clarity.
Below, we describe a general method useful for the analysis of differential EXAFS data of small metal nanoclusters and provide a quantitative assessment of the restructuring of the Pd NCs. The EXAFS signal $\chi(k)$ for modeling the first shell scattering of nanocluster sample, with two types of bonds, core ($i$) and surface ($i'$), is shown in below (prime refers to surface bonds):

$$
\chi(k) = \frac{s_0^2 N_i f(k) e^{-2r_i \lambda(k)} e^{-2k^2 \sigma^2}}{kr_i^2} \sin(2kr_i + \delta(k)) + \frac{s_0^2 N_i' f(k) e^{-2r_{i'} \lambda(k')} e^{-2k^2 \sigma'_{i'}}}{kr_{i'}^2} \sin(2kr_{i'} + \delta(k))
$$

where $k$ is the photoelectron wave number, $S_0^2$ is the passive electron reduction factor, $f(k)$ and $\delta(k)$ are the photoelectron scattering-path amplitude and phase, respectively, $N$ is the coordination number, $r$ is the interatomic distance, $\sigma^2$ is the mean-square deviation in $r$, and $\lambda(k)$ is the photoelectron mean free path. Correspondingly, the EXAFS equation for the “Clean Pd NCs” sample, $\chi_{\text{clean}}$, is:

$$
\chi_{\text{clean}}(k) = \frac{s_0^2 N_i f(k) e^{-2r_i \lambda(k)} e^{-2k^2 \sigma^2}}{kr_i^2} \sin(2kr_i + \delta(k)) + \frac{s_0^2 N_i' f(k) e^{-2r_{i'} \lambda(k')} e^{-2k^2 \sigma'_{i'}}}{kr_{i'}^2} \sin(2kr_{i'} + \delta(k))
$$

The EXAFS equation for the "After Ar adsorption" sample, $\chi_{\text{After}}$, is:

$$
\chi_{\text{After}}(k) = \frac{s_0^2 N_2 f(k) e^{-2r_2 \lambda(k)} e^{-2k^2 \sigma^2}}{kr_2^2} \sin(2kr_2 + \delta(k)) + \frac{s_0^2 N_2' f(k) e^{-2r_{2'} \lambda(k')} e^{-2k^2 \sigma'_{2'}}}{kr_{2'}^2} \sin(2kr_{2'} + \delta(k))
$$
Since the interior atoms are unchanged during the Ar adsorption, $N_1 = N_2$, $r_1 = r_2$, and $\sigma_1^2 = \sigma_2^2$. In addition, $S_0^2$, $f(k)$, and $\lambda(k)$ will be identical in all terms since they all refer to a Pd-Pd single scattering path. The number of surface atoms, $N_s$, or $N_{s'}$, will also remain unchanged and this will be referred to as $N_s$. If Eq. (3) is subtracted from Eq. (2), the following expression is derived for $\Delta$-EXAFS ($\chi_{\text{Clean}} - \chi_{\text{After}}$):

$$\Delta\text{-EXAFS} = S_0^2 N_s f(k) e^{-\frac{2r_1'}{k}} e^{-2k^2 \sigma_1'^2} \frac{1}{k r_1'^2} \sin(2kr_1' + \delta(k)) -$$

$$S_0^2 N_s f(k) e^{-\lambda(k)} e^{-2k^2 \sigma_1'^2} \frac{2(r_1' + \Delta r)}{k(r_1' + \Delta r)^2} \sin(2k(r_1' + \Delta r) + \delta(k)) \quad (4)$$

where $r_2$, is expressed as $r_1 + \Delta r$. We note that Eq. (4), in the approximation that the bond length disorder did not change between the two states, and that $\Delta r \ll r$, reduces to a simple ansatz (a complete derivation of Eq. 5 is provided in the supplementary information):

$$\Delta\text{-EXAFS} \approx S_0^2 N_s f(k) e^{-\frac{2r_1'}{k} \lambda(k)} e^{-2k^2 \sigma_1'^2} (2k \Delta r) \sin \left( 2kr_1' + \delta(k) + \frac{\pi}{2} \right) \quad (5)$$

Thus, Eq. (5) shows that for small variations in the bond length, $\Delta r$, the differential EXAFS spectrum will display a $\pi/2$ phase shift compared to the original EXAFS spectrum ($\chi_{\text{Clean}}$). This validates our conclusions based on visual examination of the $\Delta$-EXAFS (Figure 5-3) which also shows the $\pi/2$ phase shift compared to the spectrum measured in He or Ar atmospheres. We note that Eq. (5) is equivalent to that used for analysis of differential signal in magnetostriction experiment by modulation excitation method.$^{18}$

The differential spectrum can be modeled by implementing Eq. (4) into a suitable data analysis program. In this work it was accomplished by using FEFF models for each spectrum and
fitting the difference between the two modeled signals to the experimental data. The total number of Pd-Pd bonds affected by Ar adsorption, $n_{PD-PD,aff}$, can be estimated directly from the measured $N_s$, the coordination number of Pd-Pd atoms in the differential spectrum, and the total number of atoms in a representative particle (n) as follows:

$$N_s = \frac{2n_{PD-PD,aff}}{n} \quad (6)$$

We note that the denominator is the total number of atoms per particle, not the total number of affected atoms, which would make it analogous to a conventional expression for coordination number because the differential signal was obtained by subtracting the edge-step normalized EXAFS spectrum. Edge step normalization is the procedure that relates the total EXAFS signal from all absorbing atoms in the sample to that corresponding to an “an equivalent absorber”, hence, the total number of atoms is used in the denominator of Eq. (6).

The terms $r_1$ and $\sigma^2_1$ were obtained from the fit of the “Clean Pd NCs” (Figure 5-1 and Table 5-1) under the approximation the surface atoms have a bond length and EXAFS Debye-Waller factor equivalent to the bulk value of the Pd NCs (i.e. $r_1 = r_{1'}$ and $\sigma^2_1 = \sigma^2_{1'}$) However, in other cases, higher data quality may allow for the determination of $r_{1'}$ and $\sigma^2_{1'}$ directly from the differential data.

The results of fitting the $\Delta$-EXAFS with Eq. 4 are presented in Table 5-2 and the Fourier transform magnitude EXAFS for the data and the fit are presented in Figure 5-4. The number of Pd-Pd bonds that changed during the Ar-induced restructuring is $9 \pm 2$. These bonds expanded by $\Delta r = 0.104 \pm 0.005$ Å. In addition, the disorder of these bonds decreased since the EXAFS Debye-Waller factor decreased from $0.0088 \pm 0.0002$ to $0.0045 \pm 0.0009$. Thus, the EXAFS analysis shows that $9 \pm 2$ NN Pd-Pd bonds expand as a result of introducing Ar at 77 K. This is compared to the total number of NN Pd-Pd bonds in a 37-atom Pd cluster of 129.
Table 5-2. Fit parameters obtained from the differential data using Eq. (4).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Allowed to Vary?</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_s$</td>
<td>0.46 ± 0.07</td>
<td>Yes</td>
</tr>
<tr>
<td>$r_{1}'$</td>
<td>2.700 ± 0.005 Å</td>
<td>No\textsuperscript{a}</td>
</tr>
<tr>
<td>$\sigma_{1}'^2$</td>
<td>0.0088 ± 0.0002</td>
<td>No\textsuperscript{a}</td>
</tr>
<tr>
<td>$\Delta r$</td>
<td>0.104 ± 0.005 Å</td>
<td>Yes</td>
</tr>
<tr>
<td>$\sigma_{2}'^2$</td>
<td>0.0045 ± 0.0009</td>
<td>Yes</td>
</tr>
<tr>
<td>$n_{Pd-Pd,aff}$</td>
<td>9 ± 2</td>
<td>\textsuperscript{b}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Obtained from fit of Clean Pd NCs.
\textsuperscript{b}Determined after the fit using Eq. (6), where $n = 37$. 
Figure 5-4. Fourier transform magnitude of $k^2$-weighted $\chi(k)$ for the $\Delta$-EXAFS spectrum (black) and the fit of the data (blue) using the model in Eq. (4).
EXAFS analysis by fitting method often depends on the model used, and comparing several models is necessary to avoid possible misinterpretation of the data. We have compared two additional models that are described below. The first model was a Pd-Ar single-scattering model that assumes that the differential signal could arise from Pd-Ar scattering only. Attempts to fit the $\Delta$-EXAFS signal with the Pd-Ar scattering model (Table S5-1 of the supplementary information) results in an unrealistic fit parameter for the energy shift and a poor-quality fit to the data. Therefore, we dismiss the possibility that the differential signal arises from Pd-Ar contributions. The second model was a direct fit of the differential data with Pd-Pd scattering (Table S5-2 of the supplementary information). This model would only be appropriate if the number Pd-Pd bonds changed, such that the amplitude of the differential data represents additional Pd-Pd bonds that arose during the adsorption of Ar (or Pd-Pd bonds that were removed during the adsorption). Fitting the differential data with this model results in a good fit to the data, and the Pd-Pd bond length expansion was comparable to what was found in the present differential model EXAFS model. However, this model is under the presumption that the overall Pd-Pd coordination number changed during Ar adsorption. On the other hand, the differential EXAFS model described in Eq. (4) shows that the differential EXAFS signal arises from a change in bond length only, with no change in the overall Pd-Pd coordination number. Thus, using EXAFS alone, it is impossible to differentiate between the two aforementioned models. We will show through the atomistic modeling described below that we are able to use theory to break the degeneracy of the two competing EXAFS models.

4.3.2. Atomistic Modeling of Ar-induced Restructuring

To support our experimental observation of Ar-induced surface restructuring of Pd atoms and to differentiate between the proposed EXAFS models, we conducted a series of ReaxFF-MD simulations in which model Pd clusters were exposed to both vacuum and an Ar gas phase (i.e. 50
Ar atoms in the periodic cell) at 77 K. In each simulation, the average Pd-Pd bond distance was assessed from the atomic coordinates of the system, thus allowing changes in average Pd-Pd bond distance after the introduction of Ar atoms to be determined. Figure 5-5 depicts the initial and final system geometries in an MD simulation where a 1 nm Pd cluster was exposed to Ar. As seen in the figure, Ar interacts weakly with the cluster, forming a physisorbed layer of Ar atoms on the surface of the cluster. The calculated adsorption energy for an isolated Ar atom on Pd is 1 - 2 kcal mol$^{-1}$, which is dependent on the adsorption configuration.
Figure 5-5. (a) Initial and (b) final system geometry in a 1 ns MD-NVT simulation at 77 K. (c) Pd-Ar radial pair distribution function, $g(r)$, demonstrating an Ar physisorption well centered near $r = \sim 3.9$ Å from the cluster surface.
To assure modeling results were not biased by the initial selection of cluster geometry, we employed a hybrid MC/MD simulation method to generate a set of model Pd clusters. The MC/MD simulation was conducted at 500 K, which corresponds to the experimental annealing temperature the Pd clusters were exposed to before being quenched to 77 K. This results in an ensemble of cluster geometries that are representative of those present in the experimental sample, where the energy differences between clusters arise due to thermal fluctuations in the system, as shown in Figure 5-6. The model clusters do not include the SiO₂ support used experimentally, and therefore we neglect any effect the support could have on initial Pd nanocluster structure or the restructuring process. The relative impact of this simplification is further addressed in the discussion section.
Figure 5-6. Energy of clusters generated from a hybrid MC/MD simulation at 500 K. The green and red data points indicate clusters that were selected for separate MD simulations to assess Pd-Pd expansion upon exposure to Ar. Green diamonds indicate that an average Pd-Pd expansion $>0.001$ Å was observed and red dots indicate that there was no change $>0.001$ Å.
We selected 50 clusters (using a random number generator) from the 500 K MC/MD sample set to serve as starting geometries for MD simulations at 77 K. The selected clusters correspond to the green and red data points in Figure 5-6. During each 77 K MD simulation, average Pd-Pd bond distances were determined by calculating the Pd-Pd radial pair distribution, \( g(r) \), over the last 250 ps of the 1 ns MD simulations. As shown in Figure 5-7 for a single cluster geometry, each simulation initially allows the Pd cluster to equilibrate at 77 K for 1 ns in vacuum before exposure to Ar (or He/vacuum in the case of control simulations). As seen in the figure, the simulation yields no change in Pd-Pd bond distance after exposure to vacuum or He, whereas cluster restructuring with a 0.003 Å Pd-Pd expansion occurs under Ar. The radial distribution function in Figure 5-7(d), in comparison to those for control simulations in Figure 5-7(a-c), demonstrates a clear restructuring of the cluster, where the shoulder appearing at \( r = \sim 2.60 \) Å in the control simulations shifts to \( r = \sim 2.75 \) Å (indicated by black arrows in the figure). This suggests the average Pd-Pd bond expansion can be attributed to a large increase in a few Pd-Pd bonds involving one or two atoms, as opposed to a small increase in all Pd-Pd bonds throughout the cluster. This is further depicted in Figure 5-8, which shows snapshots from the 15 ps MD-trajectory window in which the surface restructuring occurs. The restructuring occurs immediately after the Pd cluster interacts with an incoming Ar atom, suggesting that the momentum transfer from the Ar atom to the cluster induces the surface reconstruction. This reconstruction does not occur in the absence of the Ar gas phase. An animated video of this 15 ps trajectory demonstrating surface reconstruction is provided in the supplementary information, along with a 250 ps video of the cluster in vacuum showing no reconstruction.

A similar analysis was conducted for all 50 model clusters, where 8 clusters demonstrated an average Pd-Pd bond length expansion greater than 0.001 Å upon exposure to Ar and the remaining 42 exhibited no change greater than 0.001 Å, indicated by green diamonds and red dots, respectively, in Figure 5-6. The expansion of Pd-Pd bond lengths was further quantified by assessing the average Pd-Pd bond length change for a single Pd atom as a function of its average
coordination number under vacuum conditions. This is shown in Figure 5-9, where we have plotted average bond length expansion against coordination number in vacuum averaged over all 50 clusters investigated. Figure 5-9(a) contains data from clusters that exhibited an expansion, while Figure 5-9(b) contains data from clusters that did not exhibit expansion. This analysis reveals that only under-coordinated Pd atoms with low nearest-neighbor coordination numbers (i.e., 3-5) are affected by the Ar adsorption, with a typical bond length expansion of ca. 0.05 to 0.1 Å. Figure 5-9(b) demonstrates some under-coordinated atoms are not affected by the Ar gas phase, indicating that some under-coordinated atoms are more stable than others. Observed coordination numbers greater than 12 reflect that these clusters have a disordered, non-crystalline lattice structure, which is expected for platinum-group-metals in this size range.32
Figure 5-7. Pd-Pd radial distribution function, $g(r)$, reflecting the average NN Pd-Pd bond distances during a 1 ns MD simulations at 77 K. (a) The Pd cluster was first allowed to equilibrate in vacuum for 1 ns, and was then exposed to (b) vacuum, (c) He gas, or (d) Ar gas for an additional 1 ns. Arrows indicate the peak shift attributed to the average Pd-Pd bond expansion of an under-coordinated surface atom.
Figure 5-8. A 15 ps MD trajectory window demonstrating an Ar (green) collision with a Pd cluster (blue) inducing the restructuring of an under-coordinated Pd surface atom (purple). Only the Ar atom interacting with the Pd cluster is shown, all others are omitted for clarity.
Figure 5-9. Bond length expansion (relative to the clusters in vacuum) plotted versus first shell coordination number for all of the atoms in each of the Pd clusters that (a) exhibited expansion and (b) did not exhibit expansion after exposure to Ar at 77 K. Error bars indicate the standard deviation in bond length of the ensemble of atoms from each of the clusters.
Since Ar induces restructuring of under-coordinated surface atoms, it is likely that these atoms are kinetically trapped in metastable positions during the quench to 77 K, and that a transfer of kinetic energy from an Ar gas phase atom provides the additional energy required to allow relaxation of the metastable Pd atom to a more favorable site with higher average coordination and longer average Pd-Pd bonds. Not all under-coordinated sites are affected by Ar which could be the result of short simulation timescales, where a sufficient Pd-Ar interaction simply never occurred in the simulation timeframe. Also, some under-coordinated sites may be more stable than others, indicating that Ar can only induce the restructuring of sufficiently unstable Pd atoms. A ReaxFF nudged-elastic-band (NEB) barrier calculation, provided in the supplementary information (Figure S5-4), yielded a barrier of 11.4 kcal mol\(^{-1}\) for the reconstruction shown in Figure 5-8, which is sufficiently high to suggest that this structure would be kinetically stable at 77 K under vacuum. Together, these simulations demonstrate that Ar may drive surface reconstructions of under-coordinated atoms, thus leading to an increased Pd-Pd bond length of surface Pd atoms, in agreement with the experimental observations above.
5.4. Discussion

Analysis of the differential EXAFS data using the model in Eq. (4) shows that Ar adsorption on Pd/SiO$_2$ at 77 K induces small changes in the Pd-Pd coordination environment, which can be attributed to the expansion in the bond length of surface Pd atoms. However, this model was created under the presumption that the overall Pd-Pd coordination number remained unchanged during Ar adsorption, and the correctness of such an approximation can be verified by examining simulated clusters before and after Ar adsorption. We calculated the average Pd-Pd coordination number of the clusters shown in Figure 5-9(a) before and after Ar adsorption. The results are presented in Table 5-3. In each of the 8 simulations in which Ar caused restructuring, under-coordinated Pd atoms formed new Pd-Pd bonds, which is concomitant with expansion in their bond length. The number of Pd-Pd bonds formed varied, as this is dependent on the starting structure. Meanwhile, a similar number of Pd-Pd bonds were broken such that the average change in Pd-Pd coordination number was ~0. Therefore, the atomistic simulations are in agreement with the proposed differential EXAFS model in Eq. (4) and the experimental results shown in Table 5-2.
Table 5-3. Coordination environment changes of Pd clusters as a result of Ar adsorption.

<table>
<thead>
<tr>
<th>Simulation&lt;sup&gt;a&lt;/sup&gt;</th>
<th># of Pd-Pd bonds formed&lt;sup&gt;b&lt;/sup&gt;</th>
<th># of Pd-Pd bonds broken&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Δ avg NN CN&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.2</td>
<td>-9.6</td>
<td>-0.06</td>
</tr>
<tr>
<td>2</td>
<td>9.0</td>
<td>-9.8</td>
<td>-0.02</td>
</tr>
<tr>
<td>3</td>
<td>3.2</td>
<td>-1.3</td>
<td>0.04</td>
</tr>
<tr>
<td>4</td>
<td>5.1</td>
<td>-3.0</td>
<td>0.05</td>
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<td>5</td>
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</tr>
<tr>
<td>6</td>
<td>4.5</td>
<td>-1.1</td>
<td>0.08</td>
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<tr>
<td>7</td>
<td>3.0</td>
<td>-5.0</td>
<td>-0.05</td>
</tr>
<tr>
<td>8</td>
<td>2.7</td>
<td>-7.1</td>
<td>-0.10</td>
</tr>
<tr>
<td><strong>Averages</strong>&lt;sup&gt;e&lt;/sup&gt;</td>
<td><strong>5.1</strong></td>
<td><strong>-4.7</strong></td>
<td><strong>0.01</strong></td>
</tr>
</tbody>
</table>

<sup>a</sup>Simulations in which Ar caused restructuring.

<sup>b</sup>Number of Pd-Pd bonds formed during Ar adsorption.

<sup>c</sup>Number of Pd-Pd bonds that were broken during Ar adsorption.

<sup>d</sup>Average nearest-neighbor coordination number after Ar adsorption minus the average nearest-neighbor coordination number under vacuum.

<sup>e</sup>Average over simulations 1-8.
It is intuitive to suggest that restructuring without an overall coordination number change requires strongly disordered nanoclusters because restructuring of a faceted particle will always lead to either an increase or decrease in coordination number if the total number of atoms in the particle remains the same. McKenna and Shluger showed that faceted Au nanoparticles restructure under CO adsorption, leading to an increase in coordination number.\textsuperscript{33} Thus, for our theoretical models to be compatible with those real clusters used in our experiments, it is advantageous to model strongly disordered Pd/SiO\textsubscript{2} NCs rather than faceted, crystalline, structures. Experimentally it has been demonstrated that alumina- and carbon-supported Pt clusters are predominantly non-crystalline in the size range less than 1-1.5 nm.\textsuperscript{32}

The high effective pressure of Ar and omission of SiO\textsubscript{2}-supported Pd NCs from the theoretical portion of this study are limitations in obtaining quantitative results of the restructuring. We expect that introduction of the SiO\textsubscript{2} support might result in a different distribution in Pd particle shapes and the time scale for energy transfer from Ar to Pd could be impacted by dissipation into the support. However, the overall mechanism for restructuring is likely independent of support, since the exposed Pd atoms in low coordination environments present on the Pd particle exterior, which participate in the observed restructuring, would likely not be adjacent to the support. Furthermore, the large difference in masses between Pd and SiO\textsubscript{2} atoms suggest a low amount of vibrational coupling, and therefore we could expect that dissipation of kinetic energy passed from Ar to Pd may remain in Pd related modes on the time scale observed in simulation. Thus, atomistic modeling qualitatively supports the hypothesis that under-coordinated surface atoms are those affected and helps us gain an atomistic level understanding of the process.

Other examples of Ar-induced restructuring include the work of Pellenq et al. who measured the neutron diffraction of \textsuperscript{40}Ar adsorption in silicate-1 zeolite and showed that a step in the Ar isotherm coincides with a change in the neutron diffraction pattern.\textsuperscript{34} Using grand canonical Monte Carlo simulations (GCMC), the authors concluded the change in diffraction
pattern can be attributed to a rearrangement of the adsorbed phase. This conclusion has been further substantiated by García-Pérez et al., who showed through GCMC simulations that a flexible host structure is likely responsible for the stepped Ar isotherm at 77 K of MFI zeolite.\textsuperscript{35} More recently, Mallon et al. surmised that the hysteresis of the Ar 87 K adsorption isotherm of silicate-1 is a result of an orthorhombic-monoclinic symmetry shift.\textsuperscript{36} On the other hand, Ar ion bombardment at low energy (c.a. 15 eV) has been shown to heal defects of carbon nanotubes.\textsuperscript{37}

The EXAFS differential data analysis method we show in this paper is applicable to other systems where only a small fraction of surface species (active species) respond to the external stimulation (e.g. gas, pH, electric potential, temperature, etc.) while the majority of the atoms (spectators) are unaffected. In this study, we are able to measure a change in coordination environment of only 7\% of the total number of Pd atoms, which highlights the sensitivity of the combined measurement and analysis scheme.
5.5. Conclusions

Differential extended X-ray absorption fine structure (Δ-EXAFS) and atomistic molecular dynamic simulations have been used to detect under-coordinated surface Pd atoms of SiO$_2$-supported nanoclusters. The increased sensitivity of Δ-EXAFS allows for detection of small changes in the coordination environment of surface Pd atoms that would otherwise go undetected with conventional XAS techniques. Differentiating between possible models, a common problem associated with EXAFS analysis, was accomplished through analysis of the simulation results. Further theoretical modeling of supported clusters might provide quantitative comparison between experiment and theory.

Using an inert gas such as Ar to probe surface atoms may be advantageous over conventional surface probe molecules such as CO, NO, and H$_2$ because it physically adsorbs without specificity, different from the highly selective binding associated with chemical adsorption. In this regard, inert gas adsorption might prove to be a general method for determining surface composition of multimetallic catalysts. We also note the possibility of using Δ-EXAFS at the Ar K-edge or Kr K-edge to probe metal surfaces from the perspective of the inert gas.
5.6. References


5.7. Supplementary Information

5.7.1. Derivation of Eq. (5)

Eq. (4) is shown below:

$$\Delta \text{EXAFS} = \frac{S_0^2 N_s f(k) e^{-2kr_1'}}{kr_1'^2} [\sin(2kr_1' + \delta(k)) - \sin(2k(r_1' + \Delta r) + \delta(k))]$$

Under the approximation that the bond length disorder does not change between the two states ($\sigma_r^2 = \sigma_r'^2$), and that $\Delta r \ll r$, we get the following equation:

$$\Delta \text{EXAFS} = \frac{S_0^2 N_s f(k) e^{-2kr_1'}}{kr_1'^2} \left[ \sin(2kr_1' + \delta(k)) - \sin(2k(r_1' + \Delta r) + \delta(k)) \right]$$

Using the sum-to-product trigonometric identity ($\sin \alpha + \sin \beta = 2 \sin \frac{\alpha + \beta}{2} \cos \frac{\alpha - \beta}{2}$), Eq. 4b becomes

$$\Delta \text{EXAFS} = \frac{S_0^2 N_s f(k) e^{-2kr_1'}}{kr_1'^2} \left[ 2 \sin(k\Delta r) \cos(2kr_1' + \delta(k)) \right]$$

Since $\cos(\alpha) = -\sin \left( \alpha + \frac{\pi}{2} \right)$, equation (5) is equivalent to

$$\Delta \text{EXAFS} = -\frac{S_0^2 N_s f(k) e^{-2kr_1'}}{kr_1'^2} \left[ 2 \sin(k\Delta r) \sin \left( 2kr_1' + \delta(k) + \frac{\pi}{2} \right) \right]$$
For a small difference in bond length change, \( \sin(k\Delta r) \sim k\Delta r \), hence,

\[
\Delta\text{EXAFS} = -\frac{S_0^2 N_s f(k)e^{\frac{-2r}{\lambda k^2 r_{e}^2}}}{kr_{i}^2}(2k\Delta r) \sin\left(2kr_{i} + \delta(k) + \frac{\pi}{2}\right)
\]  

(5)
5.7.2. Supplementary Tables and Figures

Figure S5-1. Photo of specially designed *in situ* reactor. The sample is packed into the steel cylindrical holder in the center of the liquid nitrogen vacuum-insulated flask. Heating is accomplished outside the flask with heat tape and the sample can be moved from the cooled zone to the heated zone with a magnet.
Figure S5-2. $k^2$-weighted $\chi(k)$ EXAFS data for the clean Pd NCs and the Pd NCs after Ar adsorption and purging at room temperature (RT) with He. The difference shows no oscillatory behavior. The data are shifted vertically for clarity.
Figure S5-3. XANES spectra for the clean Pd NCs (green), after Ar adsorption (red), and the reference Pd foil (blue).
Table S5-1. Fit parameters obtained from the differential data using a Pd-Ar scattering model.

<table>
<thead>
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<th>Value</th>
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</thead>
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</tr>
<tr>
<td>$r$</td>
<td>3.09 ± 0.06 Å</td>
</tr>
<tr>
<td>$\sigma^2$</td>
<td>-0.0009 ± 0.002</td>
</tr>
<tr>
<td>$N$</td>
<td>0.39</td>
</tr>
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</table>
Table S5-2. Fit parameters obtained from the differential data using a Pd-Pd scattering model under the assumption the Pd-Pd coordination number is changing.

<table>
<thead>
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<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
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<td>$2.82 \pm 0.02$ Å</td>
</tr>
<tr>
<td>$\sigma^2$</td>
<td>$-0.0045 \pm 0.0006$</td>
</tr>
<tr>
<td>$N$</td>
<td>0.57</td>
</tr>
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</table>
Figure S5-4. ReaxFF-NEB barrier for surface reconstruction. Insets depict the initial and final cluster structures, where the NEB images were obtained by linear interpolation of the atomic coordinates.
Chapter 6

Identification of Second Shell Coordination in Transition Metal Species using Theoretical XANES: Example of Ti-O-(C,Si,Ge) Complexes

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6.1. Introduction

In pursuit of highly active and selective catalytic materials, it is necessary to precisely characterize the site responsible for catalytic turnover. X-ray absorption near edge structure (XANES) is a powerful technique for determination of the oxidation state and local coordination environment of the active site in single site heterogeneous catalysts (SSHCs), among other catalytic systems.\(^1\)\(^-\)\(^6\) XANES is particularly useful for catalytic systems because of its ability to be used in situ.\(^7\) Compared to its counterpart, extended X-ray absorption fine structure (EXAFS), XANES can be performed rapidly on low weight-loading samples. However, the interpretation of XANES often requires experimental XANES spectra of model compounds for comparison, or a complete set of structural information for theoretical XANES calculations.\(^8\)\(^-\)\(^9\) In addition, XANES is generally only useful for determining first shell coordination whereas the second coordination sphere of a catalytic center can dramatically affect its reactivity. For example, the presence of second-shell Ge in Ti\(^{IV}\) or Ta\(^{V}\) epoxidation catalysts has been shown to dramatically improve the catalytic activity.\(^4\)\(^,\)\(^6\)\(^,\)\(^10\)\(^-\)\(^11\)

We report on an approach for determination of the identity of a second shell atom (Ge, Si, or C) located 3.0 to 3.5 Å from the Ti atom center in molecular titanium species (Ti[OGelPr], \(\text{Ti}[\text{OSi(OTBu)}]_4\), and \(\text{Ti}[\text{OPr}]_4\) – where isopropyl is abbreviated 'Pr) by comparing ab initio XANES calculations at the Ti K-edge with experimental spectra. The presence of features in the pre-edge XANES arising from the second shell coordination of a metal center is unexpected since
XANES is generally used only as a probe of first shell coordination geometry. Our choice of
titanium systems is motivated by the wide use of titanium-based catalysts in important industrial
processes such as the Ziegler-Natta process and epoxidation reactions using titanium silicate-1
(TS-1), for example.\textsuperscript{1, 12-13} In the latter case, XANES can differentiate between octahedral and
tetrahedral Ti\textsuperscript{IV} based on the height and position of the pre-edge peak of the Ti K-edge XANES.\textsuperscript{9}
Tetrahedral Ti\textsuperscript{IV} is responsible for high activity in epoxidation reactions,\textsuperscript{1} while octahedral Ti\textsuperscript{IV} is
generally inactive.\textsuperscript{2}

Since structural information is not available in the literature for the molecular titanium
compounds used in this study, structures were first optimized with density functional theory
(DFT) and subsequently serve as the input for the ab initio XANES calculations. The XANES
calculations require no additional user input, thus the overall approach requires only an initial
approximate structure for DFT optimization. The utility of this approach extends to other
transition metal complexes where second shell information may be obtained without the need for
EXAFS analysis. The origins of features that are used as fingerprints for C, Si, and Ge in the
second shell of Ti atom complexes were determined with DFT by examining the unoccupied
orbitals above the Fermi level.
6.2. Experimental Methods

6.2.1. Materials

Ti[O.Pr]₄ was purchased from Sigma Aldrich and used without further purification. Ti[OSi(O'Bu)₃]₄ was synthesized according to literature procedures. Ti[OGe'iPr]₄ was prepared by the addition of a THF solution of iPr₃GeOH (0.969 g, 4.43 mmol, 4.1 equiv) to a THF solution of Ti[O.Pr]₄ (0.307 g, 1.08 mmol). The mixture was stirred for 18 h at room temperature followed by removal of the solvent in vacuo at 40 °C, leaving a colorless solid.¹⁴¹H NMR (C₆D₆, 300 MHz): δ 1.56 (sept, J_HH = 7.4 Hz, 3H, CH), 1.34 (d, J_HH = 7.2 Hz, 18 H, CH₃). ¹³C(¹H) NMR: δ 18.78 (CH), 19.96 (CH₃). Anal. Calcd for C₃₆H₈₄Ge₄O₄Ti: C, 47.02; H, 9.21. Found: C, 46.97; H, 9.14.

6.2.2. X-ray Absorption Spectroscopy Measurements

X-ray absorption spectroscopy (XAS) experiments were performed at beamline X19A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (Upton, NY). Solid samples Ti[OSi(O'Bu)₃]₄ and Ti[OGe'iPr]₄ were prepared for XAS measurements by spreading the powder on a piece of polyimide tape using a clean glove. The tape was folded multiple times to achieve a uniform sample thickness. A drop of Ti[O.Pr]₄ (liquid) was placed between two sheets of polytetrafluoroethylene (51 μm thickness) to create a thin film of liquid. X-ray absorption data for Ti[O.Pr]₄ were acquired in transmission geometry with an energy range from 200 eV below to 857 eV above the Ti K-edge (4966 eV). The data for Ti[OSi(O'Bu)₃]₄ and Ti[OGe'iPr]₄ were acquired in fluorescence geometry with the same energy range. A reference Ti foil was used to calibrate the X-ray energy at 4966 eV for each spectra by setting the maximum in the first derivative of the normalized Ti foil XANES to 4966 eV. The IFEFFIT package was used
to process and analyze the data.\textsuperscript{15-16} The spectra were normalized in Athena using a pre-edge range of -150 eV to -30 eV, a normalization range of 150 to 800 eV, and a spline range in k-space of 0 to 15 Å\textsuperscript{-1}.

\section*{6.2.3. Density Functional Theory Calculations}

Geometry-optimization calculations were made using the Vienna ab initio simulation program (VASP), an ab initio total-energy and molecular dynamics program developed at the Institute for Material Physics at the University of Vienna.\textsuperscript{17-18} The core region was represented by the projector augmented wave method\textsuperscript{19} and valence electron wavefunctions were expanded in a tractable plane wave basis set. The energy cutoffs of the plane wave basis sets were 400 eV (chosen to ensure convergence of total energy with respect to energy cutoff). Valence configurations were 3p\textsuperscript{6}4s\textsuperscript{2}4d\textsuperscript{2} for Ti, 3s\textsuperscript{2}3p\textsuperscript{2} for Si, 3d\textsuperscript{10}4s\textsuperscript{2}4p\textsuperscript{2} for Ge, 2s\textsuperscript{2}2p\textsuperscript{4} for O, 2s\textsuperscript{2}2p\textsuperscript{2} for C, and 1s\textsuperscript{1} for H. Structural optimizations were performed by minimizing the forces on all atoms to below 0.02 eV Å\textsuperscript{-1}, and all calculations were non spin-polarized. All molecules were placed in a 20 Å box, such that there was no interaction between molecules. The Perdew–Wang (PW91) version of the generalized gradient approximation (GGA) was used to incorporate exchange and correlation energies.\textsuperscript{20}

Additional DFT calculations using Gaussian 09 were carried out to perform Natural Bond Orbital (NBO) analysis and for visualization of the orbitals contributing to the features in the XANES spectra. Calculations were performed using the Becke, 3-parameter, Lee-Yang-Par (B3LYP) functional\textsuperscript{21-24} with a 6-311++G** basis set which includes s and p polarization functions and two sets of diffuse functions. NBO analysis was carried out using NBO version 3.\textsuperscript{25}
6.2.4. Modeling of XANES spectra

Calculations of XANES spectra were performed using an ab initio multiple scattering code, FEFF9 (with the JFEFF GUI).\textsuperscript{26,27} FEFF9 implements a real-space Green’s function approach for calculating X-ray spectra. No adjustable parameters were used in the XANES modeling. The structural parameters used for modeling were determined by geometry optimization using VASP. The full multiple scattering (FMS) card was implemented such that all atoms in the molecule were within the FMS radius. The self-consistent potential (SCF) parameters were as follows: rfms = 4, lfms1 = 0, nscmt = 30, ca =0.2, nmix = 1. The XANES parameters were as follows: xkmax = 4, xkstep = 0.03, vixan = 0. The LDOS card was added for density of states calculation with an energy range of -15 eV to 15 eV with a Lorentzian broadening with half-width of 0.2 eV.
6.3. Results and Discussion

Ti[O'Pr]₄, Ti[OSi(O'Bu)₃]₄, and Ti[OGe'Pr₃]₄ were chosen as models for this study and have been previously reported as molecular precursors for supported titanium based catalysts.¹⁰,¹⁴,²⁸⁻²⁹ They all contain Ti tetrahedrally coordinated by O, according to Scheme 1. In this picture, all atoms past the second shell of Ti have been omitted for clarity. The identity of the second nearest neighbor is either C, Si, or Ge. The experimental Ti K-edge XANES spectra for Ti[O'Pr]₄, Ti[OSi(O'Bu)₃]₄, and Ti[OGe'Pr₃]₄ are shown in Figure 6-1.
Scheme 6-1. Connectivity of Ti-O-X (X=C, Si, or Ge) complexes.\textsuperscript{a}

\textsuperscript{a}All atoms past the second shell of Ti have been omitted for clarity.
Figure 6-1. Experimental XANES spectra at the Ti K-edge for (a) Ti[O'Pr]₄, (b) Ti[OGe'Pr]₃, and (c) Ti[OSi(O'Bu)]₄ compared with theoretical XANES spectra calculated with FEFF9 for Ti[O'Pr]₄ (d), Ti[OGeMe]₃ (e), and Ti[OSiMe]₃ (f). The spectra are shifted vertically for clarity. The main pre-edge feature (A) is characteristic of Ti in tetrahedral symmetry with oxygen. The secondary pre-edge features (B) are unique for C, Si, or Ge in the second shell of the Ti center.
The XANES of Ti[O'Pr]₄ is consistent with spectra in the literature. The main pre-edge peak located at ~4970 eV (denoted by “A” in Figure 6-1) is characteristic of Ti in tetrahedral coordination with O and has been previously reported in the literature. The origin of this peak is a result of a dipole transition from the 1s orbital of the Ti atom to the p-component of the d-p hybridized orbital of the complex. The peak also contains a small amount of intensity as a result of the quadrupole 1s-3d transition and is often referred to as a 1s to 3d transition. There is strong overlap between the O 2p and Ti 3d orbitals as a result of the non-centrosymmetric symmetry of the tetrahedral structure. The precise location of the main pre-edge peaks are 4969.60 eV, 4969.78 eV, and 4969.66 eV for Ti[O'Pr]₄, Ti[OSi(O'Bu)₃]₄, and Ti[OGePr₃]₄, respectively. The height of the main pre-edge peaks are 0.58, 0.86, and 0.76 for Ti[O'Pr]₄, Ti[OSi(O'Bu)₃]₄, and Ti[OGePr₃]₄, respectively. The position and height of this peak was determined by fitting the peak with a Lorentzian function. The primary difference in the XANES between the three complexes is apparent in the range of 4972 to 4980 eV (denoted by “B” in Figure 6-1). Ti[OGePr₃]₄ displays a peak at ~4974 eV, while Ti[O'Pr]₄ has a large shoulder at ~4976 eV and Ti[OSi(O'Bu)₃]₄ shows a small shoulder at ~4976 eV.

In order to model the XANES spectra of the compounds, geometry optimized structures were first determined using DFT (Vienna ab initio simulation program, VASP). Optimized structures were used as input to FEFF9, an ab initio multiple scattering code for the calculation of XANES spectra. The structures used for geometry optimization with DFT are Ti[O'Pr]₄, Ti[OSiMe₃]₄, and Ti[OGeMe₃]₄. The structures Ti[OSiMe₃]₄ and Ti[OGeMe₃]₄ were chosen for modeling instead of the full structures of the experimental compounds Ti[OSi(O'Bu)₃]₄ and Ti[OGePr₃]₄ to reduce the computational time for geometry optimization and XANES computation. The structural parameters determined from geometry optimization are displayed in Table 6-1. The Ti-O bond length is ~1.82 Å for all three complexes. The average Ti-X (X = C, Si, or Ge) distance is the shortest for Ti-O-C (3.116 Å), followed by Ti-O-Si (3.383 Å), and the longest is for Ti-O-Ge (3.480 Å). The Ti-O-X (X = C, Si, or Ge) bond angles range from 140.9°
to 165.6° for each of the bonds in the three compounds. The Ti-O bond lengths and Ti-O-X bond angles are comparable to similar compounds reported in the literature, such as Ti(O'Bu)[OSi(O'Bu)₃]₃ which exhibits Ti-O bond distances ranging from 1.734 to 1.810 Å and Ti-O-Si angles from 151.11 to 162.72°.³³ The theoretical XANES spectra that have been calculated with FEFF9 are displayed in Figure 6-1. There is good agreement between the theoretical XANES spectra and the experimental XANES spectra. The positions of the main pre-edge features at ~4970 eV are consistent between theory and experiment. The peaks in the range of 4972 to 4980 eV are also recovered in the theoretical XANES spectra and are of great interest because each ligand (i.e. -OC, -OSi, and -OGe) has a unique signature in this region of the pre-edge XANES. The intensities of the main pre-edge features are consistently higher in the calculated spectra compared to experiment, with significant disagreement in the case of Ti[O'Pr]₄. These differences in the calculated and experimental intensities of the Ti K pre-edge features are expected as a result of instrumental broadening factors, the broadening-effect of the Ti core-hole width, uncertainties in the calculated scattering potentials, and disorder in the samples that is unaccounted for by the calculations.⁹ Disorder may play a particularly high role in Ti[O'Pr]₄ which was examined in the liquid state.
Table 6-1. Structural parameters for compounds after DFT geometry optimization.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(\text{Ti[OiPr]}_4) Å or °</th>
<th>(\text{Ti[OSiMe}_3\text{]}_4) Å or °</th>
<th>(\text{Ti[OGeMe}_3\text{]}_4) Å or °</th>
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<td>Ti-O1</td>
<td>1.809</td>
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<td>(\angle)Ti-O4-Si4 141.4</td>
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<td>av (\angle)Ti-O-Si 154.0</td>
<td>av (\angle)Ti-O-Ge 147.7</td>
</tr>
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</table>

\textsuperscript{a}Complete structural information may be found in the supplementary information.
To better understand the origin of these three peaks, we examined the FEFF9-calculated partial density of states for the complexes. Selected partial density of states for Ti[OGeMe$_3$]$_4$ are shown in Figure 6-2 along with the calculated XANES spectra of Ti[OGeMe$_3$]$_4$. At the Fermi level, referenced as 0 eV, the onset of absorption is seen in the calculated XANES spectra. Two peaks in the O p-DOS and the Ti d-DOS at ~1-2 eV coincide with onset of absorption and the main pre-edge peak in the XANES. These two peaks are a result of the crystal field splitting of the tetrahedral Ti center and correspond to the unoccupied Ti $d_{x^2}$ and $d_{x^2-y^2}$ orbitals interacting with the O 2p orbitals. The Ti p-DOS exhibits high similarity to the Ti K-edge XANES since, at the K-edge, the 1s to 4p electronic transition is being probed and it is clear that there is mixing between the Ti p-DOS and the $d_{x^2}$ and $d_{x^2-y^2}$ orbitals. The peak in the XANES at 6 eV is paired with a peak in the Ge s-DOS at the same location. There is also an increase in density of the O p-DOS at 6 eV which suggests that a hybrid orbital exists that contains Ge s-character, O p-character, and Ti p-character.
Figure 6-2. Theoretical Ti K-edge XANES for Ti[OGeMe₃]₄ and corresponding partial density of states for O p-DOS, Ti d-DOS, Ti p-DOS, and Ge s-DOS. The energy is relative to the Fermi level (-7.725 eV) calculated with FEFF9. The spectra are shifted vertically for clarity.
A simplified molecular orbital diagram for Ti[OGeMe$_3$]$_4$ was calculated using DFT and Natural Bond Orbital (NBO) analysis and is shown in Figure 6-3. NBO analysis projects the complex electronic density calculated from DFT onto an orthonormal set of Natural Atomic Orbitals (NAOs). NBO reduces the number of unoccupied orbitals near the Fermi level as compared to the B3LYP 6-311++G** Gaussian 09 calculation. The calculated orbitals for Ti[OGeMe$_3$]$_4$ near the Fermi level are shown in Figure 6-3. The HOMO is the O 2p filled nonbonded orbital at -6 eV. A band is shown due to the four equivalent orbitals each with a slightly different energy. The LUMO is the Ti unfilled nonbonded d$_{x^2}$ at 0 eV, with the d$_{x^2-y^2}$ orbital being slightly higher in energy. The next highest orbital is the Ge-O antibonding orbital, which is also shown as a band due to the four equivalent orbitals. The Ge-O antibonding orbital is 5.8 eV higher in energy than the d$_{x^2-y^2}$ orbital. This energy separation is equivalent to the energy separation between the main pre-edge peak and the secondary pre-edge peak in the XANES of Ti[OGeMe$_3$]$_4$. From visualization of the Ge-O antibonding orbital, it is clear that it points toward and adds (unoccupied) electronic density to the Ti atom. From this, along with the analysis of the DOS, we conclude that the unique features in the Ti K-edge XANES spectra from 4972 to 4980 eV are a result of the O-X (X=C, Si, or Ge) antibonding orbitals, with their energetic position and absorption intensity varying with X as indicated by the agreement of FEFF9 with experiment. It is important to note that the XANES experiment corresponds to an excited state which features a partially screened core hole, while the DFT calculations do not include such screening. However, previous work has shown for TiCl$_4$ that creation of a Ti 1s core hole changes d-orbital energy splittings by less than 0.2 eV. Thus, the small energy displacement associated with omitting core hole screening is not likely sufficient to cause a change in orbital assignment.
Figure 6-3. Molecular orbital diagram for Ti[OGeMe₃]₄, calculated using Gaussian 09 with a 6-311++G** basis set using Natural Bond Orbital analysis. Ti (white), Ge (blue), O (red), and C (gray) are shown along with electronic orbitals at each energy level plotted with an isovalue of 0.05. Distant atoms were omitted from each of the structures for clarity. The Ge-O antibonding orbital and the filled O nonbonded orbitals are shown as bands due to the dispersion in energy of four equivalent orbitals in each case.
While there are few reports in the literature regarding the use of XANES for the identification of second shell coordination in transition metal compounds, XANES has been used to examine the second shell coordination of $\text{Zn}^{2+}$ ions in solution. A feature in the XANES spectrum was attributed to the second shell coordination sphere in water that is not present in methanol. The feature was recovered with molecular dynamics and XANES calculations and attributed to the additional solvent molecules that are present in the second shell of Zn$^{2+}$ solvated by water. Similarly, the second hydration shell of Ni$^{2+}$ in aqueous solution provides a detectable contribution to XANES spectra. In other recent work, a deconvolution procedure was used to extract structural information past the first coordination shell from the XANES of lanthanoid-containing solid systems.

The combined use of ab initio DFT and theoretical XANES calculations for identification of second shell coordination is likely applicable to the analysis of other transition metal molecular complexes. The K-edge spectra of the 3d and 4d transition metal elements may be readily measured since they are at energies (4.492 - 26.711 keV) that are readily accessed at numerous synchrotron facilities. The L-edges may be measured for 5d transition metal elements to monitor the 2s - (6p or 5d) transition since the K-edge is difficult to resolve due to an increase in the core-hole broadening of spectral features at higher energies. The intensity of pre-edge features decrease as the d-orbitals are filled, which makes it difficult to resolve pre-edge features on the right side of the d-block. However, techniques such as high-energy resolution fluorescence detection XANES (HERFD) spectroscopy have shown that it is possible to gain more precise separation of weak pre-edge features from the main edge as compared to traditional XANES by detection of the radiative decay of photoexcited states. Future work is required to assess the possibility of identifying second shell coordination using XANES in other transition metal complexes.
6.4. Conclusions

DFT was used to determine the geometry-optimized structure of molecular titanium compounds that serve as the input for ab initio XANES calculations. This technique allows for the calculation of XANES spectra, which may be compared with experimental data. Ge, C, and Si atoms in the second shell of Ti coordination were identified by unique peaks in the pre-edge of the Ti K-edge XANES spectra. The O-X (X=C, Si, or Ge) antibonding orbital is responsible for an increase in the unoccupied density of states in the p-DOS of the Ti center. The combined use of ab initio DFT and XANES modeling may be used to identify second shell coordination in other transition metal complexes and provide insight into charge transfer at transition metal centers which is related to catalytic properties.
6.5. References


(33) Dhayal, V.; Chaudhary, A.; Choudhary, B. L.; Nagar, M.; Bohra, R.; Mobin, S. M.; Mathur, P. *Dalton Trans.* 2012, 41, 9439-9450.


### 6.6. Supplementary Information

#### 6.6.1. Structural Data for Geometry Optimized Structures

Table S6-1. XYZ coordinates for DFT-optimized Ti[O\(\text{Pr}\)]₄.

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Chapter 7

Conclusions and Future Work

7.1. Conclusions of the Dissertation

Isotopic labeling and DFT were used to determine the mechanism for acetylene hydrogenation and oligomerization on well-defined intermetallic nickel-zinc catalysts. The primary benefit of adding zinc to nickel is a reduction in oligomeric species formation which leads to higher ethylene selectivity. The production of ethane is not highly dependent on zinc content; therefore, ethane production is not a good descriptor of ethylene selectivity because acetylene may also be converted to higher molecular weight products. Analysis using DFT and Langmuir-Hinshelwood kinetics shows that the large decrease in the adsorption energy of acetylene on intermetallic NiZn compared to pure Ni is responsible for the observed increase in ethylene selectivity. The adsorption energy of acetylene appears to be an appropriate descriptor for carbon-carbon bond formation because a high adsorption energy leads to an increased coverage of C₂ species and an increased rate of carbon-carbon bond formation.

To determine the feasibility of creating supported intermetallic Ni-Zn nanoparticles, the structures of ZnO-supported Ni catalysts were explored with in situ X-ray absorption spectroscopy, temperature-programmed reduction, X-ray diffraction, high resolution transmission electron microscopy, scanning transmission electron microscopy, and electron energy-loss spectroscopy. Calcination of nickel nitrate on a nanoparticulate ZnO support at 450 °C results in the formation of Zn-doped NiO (ca. Ni₀.₈₅Zn₀.₁₅O) nanoparticles with the rock salt crystal structure. Subsequent in situ reduction monitored by XANES at the Ni K-edge reveals a direct transformation of the Zn-doped NiO nanoparticles to a face-centered cubic alloy, Ni₁₋ₓZnx, at ~400 °C with x increasing with increasing temperature. Both in situ XANES and ex situ HRTEM provide evidence for intermetallic β₁-NiZn formation at ~550 °C. Compared to a Ni/SiO₂ catalyst,
Ni/ZnO necessitates a higher temperature for the reduction of Ni\(^{II}\) to Ni\(^{0}\) which highlights the strong interaction between Ni and the ZnO support. The catalytic activity for acetylene removal from an ethylene feed stream is decreased by a factor of 20 on Ni/ZnO compared to Ni/SiO\(_2\). The decrease in catalytic activity of Ni/ZnO is accompanied by a reduced absolute selectivity to ethylene. H-D exchange measurements demonstrate a reduced ability of Ni/ZnO to dissociate hydrogen compared to Ni/SiO\(_2\). These results of the catalytic experiments suggest the catalytic properties are controlled, in part, by the zinc oxide support and stress the importance of reporting absolute ethylene selectivity for the catalytic semi-hydrogenation of acetylene in excess ethylene.

An in-depth examination of the γ-brass crystal structure of intermetallic Ni\(_{8+x}\)Zn\(_{44-x}\) (0 ≤ x ≤ 3) was carried out to determine the site occupancy and the coordination environment of Ni, as this material demonstrated the highest selectivity for acetylene semi-hydrogenation. For Ni\(_{8}\)Zn\(_{44}\), each Ni atom is surrounded by exactly 12 Zn near-neighbors in an icosahedral geometry. For structures with an excess of 8 Ni atoms per unit cell (but less than the solubility limit of ~11 Ni atoms per unit cell), Ni-Ni-Ni trimers form to accommodate the extra Ni in the unit cell. We used the catalytic H\(_2\)-D\(_2\) reaction to probe the effect of the bulk structure of Ni\(_{8}\)Zn\(_{44}\), Ni\(_{9}\)Zn\(_{43}\), Ni\(_{10}\)Zn\(_{42}\), and Ni\(_{11}\)Zn\(_{41}\) on the surface structure of these materials. No differences in the activation barriers of these materials for H\(_2\)-D\(_2\) exchange were observed. These results were compared with those of the Pd-Zn system, which adopts identical structures to those of the Ni-Zn system. Pd\(_{8}\)Zn\(_{44}\) shows an increased activation barrier compared to Pd\(_{9}\)Zn\(_{43}\), Pd\(_{10}\)Zn\(_{42}\), and Pd\(_{11}\)Zn\(_{41}\) suggesting that surface Pd-Pd-Pd trimers reduce the barrier for H\(_2\)-D\(_2\) exchange. The usefulness of materials derived from the γ-brass crystal structure could extend to selective catalytic reactions where active site isolation is desired.

In an effort to develop new methods to help better characterize the surfaces of catalysts, we used differential extended X-ray absorption fine structure (Δ-EXAFS) to monitor the Ar-induced surface restructuring of Pd nanoclusters (1 nm diameter, silica-supported) at 77 K. Δ-EXAFS analysis shows 9 ± 2 nearest-neighbor Pd-Pd bonds expand by 0.104 ± 0.005 Å as a
result of Ar adsorption. Atomistic molecular dynamics simulations provide evidence for a model in which Ar drives restructuring of under-coordinated Pd atoms, leading to an increased Pd-Pd bond length of surface Pd atoms with no change in overall nearest-neighbor Pd-Pd coordination number. Based on observations of the atomistic simulations, it is likely that under-coordinated atoms are trapped in metastable states at 77 K, and Ar provides the kinetic energy needed to overcome the barrier for surface restructuring. Together, experiment and theory highlight the ability of Δ-EXAFS to probe surface atoms of Pd nanoclusters.

Finally, we showed how XANES can be used to differentiate between C, Si, and Ge in the second coordination shell of Ti-O-(C,Si,Ge) molecular complexes based on differences in their Ti K-edge XANES spectra. Experimental spectra were compared with theoretical spectra calculated using density functional theory structural optimization and ab initio XANES calculations. The unique features for second shell C, Si, and Ge present in the Ti K pre-edge XANES are attributed to the interaction between the Ti center and the O-X (X=C, Si, or Ge) antibonding orbitals. Using these techniques, the structural information obtained from XANES is no longer limited to the first coordination sphere.
7.2. Future Work

7.2.1. Development of Selective and Active Ni-Based Intermetallic Catalysts

In Chapter 2, we showed that Ni-Zn catalysts are more selective than pure Ni catalysts due to a reduction in the binding energy of acetylene which reduces the tendency of the catalysts to form carbon-carbon bonds, thus increasing the overall selectivity to ethylene. The adsorption energy of hydrogen is essentially unchanged with the addition of Zn leading to Ni-Zn surfaces with a higher ratio of hydrogen:acetylene and increased selectivity compared to pure Ni. However, the most selective Ni-Zn catalyst (i.e., Ni$_5$Zn$_{21}$) has a 100-fold decrease in activity compared to pure Ni. This decrease in activity is a result of the dilution of the active Ni sites with Zn atoms which are by themselves inactive for acetylene hydrogenation.

Thus, to produce a Ni-based catalyst that is both active and selective, we hypothesize that it is required for the second metal be active for acetylene semi-hydrogenation in its pure form. Base-metal candidates for this include Fe, Co, and Cu, which dissociate hydrogen and are active for hydrogenation reactions in their pure form. At high temperatures, Ni-Cu, Ni-Fe, and Ni-Co all form complete substitutional solid solutions across the entire range of composition, according to their phase diagrams. Thus, the formation of intermetallic compounds with these materials is limited. However, at temperatures less than 500ºC, intermetallic compounds such as FeNi and FeNi$_3$ are present in the Fe-Ni phase diagram and are viable materials for further testing. Furthermore, the ternary compound, Cu$_6$Fe$_{22}$Ni$_{72}$ has been identified as a stable intermetallic structure and is also a viable material for further testing for selective hydrogenation reactions. The complete Ni-Cu-Fe phase diagram is shown in Figure 7-1. An experimental investigation and theoretical studies are required to determine the catalytic behavior of these materials.
Figure 7-1. The computed Ni-Cu-Fe ternary phase diagram at 450 °C.\textsuperscript{3}
7.2.2. Isolated Catalysts with the γ-Brass Crystal Structure

In Chapter 4, we showed the usefulness of the γ-Brass structure in the Ni-Zn system towards isolating Ni atoms. The γ-Brass structure is common to many other element pairs beyond Ni-Zn including: Ag-Cd, Ag-Zn, Al-Cu, Au-Cd, Au-Zn, Cd-Cu, Cd-Ni, Cd-Pd, Cd-Pt, Cd-Rh, Co-Zn, Cu-Ga, Cu-Sn, Cu-Zn, Fe-Zn, Ir-Zn, Mn-Zn, Pd-Zn, Pt-Zn, and Rh-Zn. The minority elements in these systems (Mn, Fe, Ni, Co, Cu, Rh, Pd, Ag, Ir, Pt, and Au) are often completely isolated by the majority element. Since the minority elements listed above are active catalysts for many different reactions, it is likely γ-brass structures produced from these elements will also be active catalysts. The actual activities and selectivities of these materials should be tested (either experimentally or theoretically) for reactions in which selectivity is required, such as selective hydrogenation reactions.

7.2.3. Probing the Surface of Bimetallic Catalysts using Kr Adsorption and X-ray Absorption Spectroscopy

Identifying the number and identity of exposed atoms on bimetallic catalyst nanoparticles is of utmost importance in understanding catalytic behavior. Pd-Ag catalysts provide a good example of why it is important to determine surface composition. Pd-Ag catalysts are widely employed industrially for the selective hydrogenation of acetylene to ethylene. Pd-only catalysts are unselective for this reaction. The role that Ag plays in increasing the selectivity is not well understood. Does the Ag coat the Pd particles to form a core-shell morphology where the Pd is prevented from directly interacting with the reactants, or does the Ag alloy with the Pd such that a small fraction of the Pd atoms are still accessible to the reactants? Answering this question will provide important insights into the structure of the Pd-Ag catalysts, which is related to their function.
Existing methods for determination of catalyst surface composition include X-ray photoelectron spectroscopy (XPS), chemical adsorption using probe molecules, and EXAFS modeling (to determine overall nanoparticle structure). XPS is unable to determine surface composition because the information depth is greater than the thickness of a single atomic layer. Chemical adsorption using CO and infrared spectroscopic techniques is commonly employed to probe the surface structure of catalysts, but is only useful for elements to which it adsorbs with known stoichiometry. In the case of alloys or intermetallics compounds, the stoichiometry of this adsorption is generally unknown. In addition, surface restructuring is possible when CO is adsorbed to a surface as a result of the strong interaction between CO and many transition metals. EXAFS modeling has recently been used to elucidate the structure of bimetallic nanoparticles, but requires a homogeneous sample (i.e. no monometallic particles, uniform particle size, and uniform particle morphology) which is often not the case with supported catalysts. In contrast, the proposed method will determine the elemental-specific dispersion accurately, regardless of the particle size homogeneity of the sample.

In Chapter 5, we showed how Δ-EXAFS can be used to probe the surface atoms of 1 nm supported palladium nanoclusters due to the rearrangement that is caused from the adsorption of Ar at 77 K. We had originally hypothesized that we could determine the Pd-Ar coordination number and relate this to the dispersion of the nanoparticles. However, we found that the movement of Ar on the surface of the Pd nanoparticles leads to a large distribution in the Pd-Ar bond lengths, which eliminates the signal of Pd-Ar scattering. This can be proven by examining the equation that describes EXAFS oscillations where $\sigma^2$ is the mean-square deviation in the bond length:

$$
\chi(k) = \frac{S_0N_{1f}N_{2s} \times \frac{2r_i}{\lambda(k)} e^{-2k^2\sigma^2}}{k r_i^2} \sin(2kr_i + \delta(k))
$$

(1)
At large values of $\sigma^2$, the magnitude of the EXAFS oscillations approaches zero.

As a variation of the experiments performed in Chapter 5, we propose the use of EXAFS-monitored Kr adsorption at 4 K for determining the surface composition of bimetallic catalysts. Operating at a lower temperature and utilizing Kr, which has a higher critical temperature than Ar, results in very little movement of Kr and a small value of $\sigma^2$. Furthermore, the binding energy of the 1s electron of Kr is 14.35 keV, which is sufficiently high to measure EXAFS at the Kr K-edge. Thus, it may be possible to determine the surface composition of multi-metallic nanoparticles from the perspective of Kr atoms on the surface. This concept is illustrated in the cartoon in Figure 7-2. More specifically, the Kr-M coordination numbers could be determined with EXAFS for all metals, M, on a multi-metallic catalyst surface. This would allow for the determination of molar percentages of each metal on the surface and the relation of elemental surface composition to catalytic behavior.
Figure 7-2. Cartoon illustrating the use of krypton (Kr) to determine the elemental surface composition of multi-metallic catalysts.
7.3. References


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Presentation award at the Pittsburgh-Cleveland Catalysis Society Spring Meeting (2013)

Publications