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Adsorption of Hydrogen onto Bare and Metal Decorated Metal Oxides

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I am submitting herewith a dissertation written by Paige Elizabeth Landry entitled "Adsorption of Hydrogen onto Bare and Metal Decorated Metal Oxides." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

John Z. Larese, Major Professor

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(Original signatures are on file with official student records.)
Adsorption of Hydrogen onto Bare and Metal Decorated Metal Oxides

A Thesis Presented for
The Doctor of Philosophy Degree
The University of Tennessee, Knoxville

Paige Elizabeth Landry
December 2011
To my parents. Thank you for everything.
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Abstract

Catalytically relevant metal clusters were deposited on metal oxide supports. Palladium and gold were deposited on mixed morphology ZnO, and palladium was deposited on MgO(100). The materials were characterized with electron microscopy, photoluminescent spectroscopy, and X-ray photoelectron spectroscopy. The behavior of hydrogen on these materials, as well as bare ZnO, was studied using volumetric isotherms. The isotherms were used to determine the monolayer gas coverage, surface area, and heats of adsorption of hydrogen on these materials over the temperature range of approximately 8-13 K. At the temperatures and pressures studied, hydrogen physically adsorbed onto the materials. Additional investigations with inelastic neutron scattering were conducted on palladium decorated ZnO and bare ZnO. These revealed that hydrogen molecules on bare ZnO act as three dimensional free rotors, but hydrogen on palladium decorated ZnO acts as a two-dimensional planar molecule and undergoes a 6.2% bond length extension.
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Chapter 1

Introduction

Metals and metal oxides play a variety of roles in everyday life, from the nanoparticles in sunblocks to industrial-scale catalytic processes that generate fuels. They often work together in catalytic processes such as hydrocarbon reforming, methanol synthesis, and carbon monoxide oxidation, where the metal oxides serve as supports for the catalytic clusters. At one time, the supports that small metal clusters were deposited onto were thought to serve primarily as a means of preventing the agglomeration that would take place if small unsupported metal particles were used. It is becoming clear that this is not accurate, and in fact the type of support that a metal particle is placed on can change the behavior of that particle. A widely cited example of this is palladium on zinc oxide, which is known to form a PdZn alloy that can boost the catalytic performance of the palladium. This work will investigate the interactions between catalytically relevant metal clusters and their metal oxide supports, and how hydrogen interacts with these materials.

The materials that are investigated here are palladium clusters on ZnO, gold clusters on ZnO, and palladium clusters on MgO, as well as bare ZnO. These allow for a comparison of how the behavior of materials changes when the support is altered, or a different metal is deposited. Characterization of these materials was carried out using electron microscopy, X-ray diffraction, photoluminescent spectroscopy, and
X-ray photoelectron spectroscopy to probe the structure of the metals and the metal oxides, as well as the electronic state of the metal clusters. The behavior of hydrogen adsorbed onto these surfaces was probed with volumetric adsorption isotherms and with inelastic neutron scattering. Isotherms can yield insight into the macroscale behavior of a system, such as the thermodynamics of adsorption. Neutrons are an unrivaled probe for investigating the behavior of hydrogen, and inelastic neutron scattering can provide information about the dynamics of hydrogen molecules. The para to ortho rotational transition of the hydrogen molecule is affected by the environment of the molecule, so the presence of multiple adsorption sites, or a particularly strong molecule-surface interaction can be detected with this probe. Hydrogen adsorbed onto surfaces may behave similarly to free hydrogen molecules, but some surfaces strongly influence the behavior of hydrogen. Metals often exhibit strong interaction with hydrogen, with a classic example of this being the dissociation of hydrogen, but this is not the only possible outcome of this interaction. An inelastic study of hydrogen on bare and palladium ZnO was conducted here and provides a clear comparison of how the behavior of this molecule is affected by the adsorption substrate. Isotherms of hydrogen on gold decorated ZnO and palladium decorated MgO provide some additional points of comparison for different hydrogen behavior on a variety of metal decorated metal oxides.
Chapter 2

Background

2.1 Materials

2.1.1 Applications of Materials

A catalyst is a material that accelerates the rate of a reaction without appearing in the final products. Catalyzed reactions on solid catalysts take place at the surface of that material, so efficiency increases with surface area. Finely divided particles are usually dispersed on an inert support material that helps prevent smaller particles from sintering into larger ones. Small particle sizes not only maximize the surface-to-volume ratio, but can also affect the selectivity of one product over another [Ertl and Freund, 1999]. Gold is an interesting case where particle size is particularly important. Bulk gold is widely known to be inert, but gold in the form of clusters smaller than 10 nm can become catalytically active in CO oxidation [Choudhary and Goodman, 2005].

Support materials are frequently metal oxides such as alumina, titania, zinc oxide, or magnesium oxide. These supports were once thought to be primarily inert, but it is widely recognized that the support can play an important role in the chemical activity of metal clusters [Xu et al., 1997], [Cubeiro and Fierro, 1998]. Supports can boost catalytic activity in a variety of ways, such as gettering impurities that could
poison catalysts, or they might actually form alloys with the metal cluster. One of the most commonly cited alloys is the formation of a PdZn alloy for palladium particles on ZnO [Iwasa et al., 1995], [Burton et al., 2008]. The activity of palladium catalysts tends to be strongly affected by the support material used, which implies that the interaction between the support and palladium alters the electronic properties of the palladium. If a metal cluster-support interface is in equilibrium, the chemical potentials must be the same. This equalization can occur through charge transfer between the two materials.

2.1.2 ZnO

ZnO is a metal oxide that is widely used in industry as a component of paints, sunblock, and in the vulcanization of rubber and as an anticorrosion coating. ZnO is a post-transition II-IV metal oxide material with a direct bandgap of 3.37 eV [Tronc and Vennegues, 2008]. ZnO exhibits several properties, including changes in electrical resistivity, semiconducting, and optical properties which can depend on the type and concentration of defects, dopants, and adsorbed molecules, that make it a useful material in additional applications including gas sensing, catalysis, and optoelectronic devices. [Henrich and Cox, 1994], [Catlow et al., 2008]. Bulk ZnO has high bulk electrical resistivity when stoichiometric, but its semiconducting properties can be tuned by oxygen loss or doping with impurities. Post transition metal oxides have less ionic character than alkaline earth oxides, and ZnO’s ionicity is borderline between a covalent and an ionic semiconductor [Ozgur et al., 2005] [Tronc and Vennegues, 2008].

At ambient conditions, wurtzite is the thermodynamically stable phase of ZnO. The wurtzite structure consists of two interpenetrating hexagonal close packed lattices, with atoms displaced from each other along the c-axis(see figure 2.1). Each cation is tetrahedrally coordinated with four anions. This tetrahedral coordination
Figure 2.1: The Wurtzite structure of ZnO. Figure (a) shows the interpenetrating lattices of zinc and oxygen [Henrich and Cox, 1994]. Figure (b) emphasized the tetrahedral coordination between Zn and O atoms [Wang, 2004].
leads to several possible surface structures. There are four low-index faces that are significant, two nonpolar and two polar faces.

Both of the nonpolar faces, (10\overline{1}0) and (11\overline{2}0), are atomically flat and have the same number of cations and anions in the surface plane. A simple bulk termination will result in what could be thought of as Zn-O dimers on the surface, with the adjacent dimers forming stripes of Zn and O atoms on the (10\overline{1}0) face, while the Zn and O atoms alternate on the (11\overline{2}0) face. The two nonpolar faces are shown in figure 2.2.

The (10\overline{1}0) face is the most stable of all of the faces, and is parallel to the c-axis. The surface is a mixed terminated face with both Zn and O atoms on the surface. SEM has shown this surface to be the predominant exposed surface when hexagonal pillars are formed [Woll, 2007], [Henrich and Cox, 1994]. The surface of this face remains very close to the face of a truncated bulk, and does not undergo major relaxations [Strunk et al., 2009].

The (11\overline{2}0) face is also a nonpolar face, but is not as stable as the (10\overline{1}0) and there are only a limited number of studies that have been performed on this face. Theoretical studies note that the (11\overline{2}0) surface structure is similar to a simple bulk termination, but with a 6% bond length decrease and a 7% tilt of the Zn-O surface dimers [Woll, 2007].

Surfaces are designated as polar if the projection of the dipole moment related to the bulk unit cell onto the surface is nonzero. In ZnO the dipole moment of the cell is directed along the [0001] direction [Kornherr et al., 2004]. The (0001) face is polar, is terminated at the surface with Zn atoms, and is often referred to as the ”zinc face.” This face varies from bulk termination because the zinc atoms relax inward by 0.2 Å to increase their coordination with the underlying oxygen atoms [Henrich and Cox, 1994].

The (000\overline{1}) face is also polar, is terminated with oxygen atoms and referred to as the ”oxygen face”. This layer does not appear to relax inward the way Zn atoms on the (0001) face do [Henrich and Cox, 1994]. The polar faces of ZnO are shown in
figure 2.3. The polar faces of ZnO are thought to be more catalytically active than nonpolar faces [Strunk et al., 2009].

Stabilization of the Polar Faces of ZnO

The polar faces of ZnO are not stable in the configuration that would result from a simple truncation of the bulk crystal. There must be some modification of these surfaces to stabilize them. P.W. Tasker categorized ionic or partly ionic crystal surfaces into three categories: Type (1) neutral surfaces with stoichiometric proportions of anions and cations at the surface, Type (2) surfaces that are charged but do not have a net dipole moment perpendicular to the surface, and Type (3) polar surfaces with a dipole moment normal to the surface. Type (3) structures have infinite surface energy, and are not stable as a simple bulk termination of the bulk structure [Tasker, 1979]. The nonpolar faces of ZnO correspond to the description of Type (1) surfaces, and the polar faces correspond to type (3). Polar surfaces are not stable, and the electrostatic dipole fields drive surface reconstruction, where the surface atoms reorganize to minimize the energy of the surface [Henrich and Cox, 1994], [Kolasinski, 2002]. However, the magnitude of the dipole moment scales with thickness, i.e. very small oxide particles may be more stable than the bulk material [Woll, 2007]. Several mechanisms have been proposed to describe how the polar faces of ZnO might be modified to reduce the net dipole moment and stabilize the surface, primarily [Phala et al., 2005] [Henrich and Cox, 1994]:

1. Reconstruction: This could involve the formation of surface ion vacancies, which may be ordered or randomly distributed.

2. Adsorption of molecules: Adsorption of impurities such as hydrogen or water onto the surface, which then dissociate into charged species such as H\(^+\) and OH\(^-\) and adsorb on O and Zn surface ions [Kornherr et al., 2004].

3. Charge transfer between faces: Electron transfer occurs for the oxygen face to the zinc face [Meyer, 2004].
Figure 2.2: The nonpolar faces of ZnO [Henrich and Cox, 1994]
Figure 2.3: The polar faces of ZnO. The (0001) face is the "Zinc face", and the (000$\bar{1}$) face is the "Oxygen face." [Henrich and Cox, 1994]
Many studies have been performed to determine how the polar faces of ZnO are stabilized, and some studies indicate zinc vacancies on the (0001) face and oxygen vacancies on the (000\bar{1}) face [Ding and Wang, 2007]. However, most do not indicate reconstruction, so charge transfer between the two polar faces may be significant for surface stabilization [Wander et al., 2001], [Nosker et al., 1970].

Morphologies of ZnO

Numerous morphologies of ZnO can be generated with a variety of synthesis techniques. The nearly endless varieties include frequently discussed configurations such as tetrapods, hexagonal pillars and needles; and also more exotic such shapes as nanoflowers, nanonails, nanocarpets, nanokites and nanosprings [Wang, 2004]. Many of these structures are grown on quartz or alumina substrates and are produced in extremely small quantities. A significant challenge is the synthesis of larger scale quantities of ZnO with consistent morphology throughout the synthesized product. In chemical vapor deposition synthesis, small changes in the flow of oxygen and argon, or modification of the composition of the source materials, lead to tetrapods with different diameter legs [Li et al., 2009]. This wide array of structures that have been reported suggests that small changes in reaction conditions can significantly impact the synthesized product.

Characterization of ZnO using Photoluminescence

Room temperature photoluminescent (PL) spectra of ZnO generally consists of a sharp UV emission associated with the band gap (the energy range between the valence band and the conduction band where no electron states exist) and one or more visible peaks due to defects and impurities [Djurisic and Leung, 2006] [Patra and Damodara Das, 2009]. Both peaks can be observed when the ZnO is excited with photons that have higher energies than the bandgap of ZnO. The UV peak appears at about 375 nm, which corresponds to the 3.37 eV bandgap of ZnO plus the exciton

10
binding energy of 60 meV. The visible portion of the PL spectra for ZnO is not well understood, and the observed visible peak may appear anywhere from the violet to the red portion (640 to 400 nm) of the (visible) spectrum. Generally, the visible peak is attributed to either intrinsic defects such as oxygen and zinc vacancies or interstitials or chemical impurities such as copper. While many explanations have been proposed that are related to the location of the visible peak, there are no clear cut or definite assignments of PL peaks to specific defect species [Catlow et al., 2008]. The most frequently discussed visible peak position is in the green range, but a blue-violet peak is the most relevant to the materials that will be discussed in section 3.1. This peak is most frequently attributed to interstitial zinc [Yang et al., 2004] [Djurisic and Leung, 2006] or oxygen vacancies [Wu et al., 2005] [Chen et al., 2005]. The changes that occur within a PL spectrum when ZnO reaction conditions are altered can provide useful information, even if the exact type of defect is not known. Variations in the photoluminescent spectrum can be observed for different nanostructures of ZnO. This may be because defect concentration is higher at the surface of ZnO than in the bulk, so surface states are a significant factor in ZnO luminescence. Different nanostructures have different surface-to-volume ratios, which could play a significant role in the observed spectra. Several studies have demonstrated that changes in ZnO nanostructure, or even changes in the diameter of wires or tetrapod legs can cause changes in the photoluminescent spectra, such as a shift in peak position, or a change in the ratio of UV to visible peak heights [Anpo and Che, 2000] [Xiong, 2010] [Djurisic and Leung, 2006] [Shalish et al., 2004]. A sample of room temperature photoluminescence spectra for several morphologies of ZnO is shown in figure 2.4.

2.1.3 MgO

Magnesium oxide, an alkaline earth oxide, is often used as a prototypical metal oxide. It has a simple rock salt structure (shown in figure 2.5) with one thermodynamically stable face, the (100) face. Heat treatment at high temperatures (950°C for 36 hours
**Figure 2.4:** Room temperature photoluminescence for several morphologies of ZnO. 1: tetrapods 2: needles 3: nanorods 4: shells 5: highly faceted rods 6: ribbons and combs. [Djurisic and Leung, 2006]
under vacuum) can ensure that the (100) face is the only exposed face. Defects and adsorbed surface impurities can be avoided by handling the MgO in an inert gas environment after the high temperature treatment. MgO is an ionic solid that is an excellent insulator, and cannot be made into a conductor through doping [Henrich and Cox, 1994]. Defect free MgO is not generally considered to be active as a catalyst or as a significant promoter of catalytic activity in deposited metals [Wachs, 2005] [Coluccia et al., 1981]. Despite this, it is still used as a support for catalytic metals in studies of catalytic activity, in part because it has a well defined (100) surface, which makes it an excellent model system [Kakkar et al., 2006].

![Figure 2.5: Rocksalt structure of MgO, shown with a model (Mg$^{2+}$ are green, O$^{2-}$ are red) and an actual image of an MgO cube.](image)

**Figure 2.5:** Rocksalt structure of MgO, shown with a model (Mg$^{2+}$ are green, O$^{2-}$ are red) and an actual image of an MgO cube.

## 2.2 Adsorption of Gasses

### 2.2.1 Forces of Adsorption

When molecules come in contact with a surface, they may physically adsorb (physisorb) or chemically adsorb (chemisorb). Physisorption refers to the weak binding of atoms or molecules to surfaces due to non-specific forces such as van der Waals interactions. Chemisorption involves much stronger binding of atoms or molecules to surfaces and occurs when the adsorption energy is large enough to be
comparable to a chemical bond [Adamson and Gast, 1997] [Bruch et al., 2007]. The boundaries between chemisorption and physisorption are not always well defined, and this is especially the case for adsorption onto metals [Steele, 1993]. Chemisorption often involves activation energies, which means that chemisorption and physisorption can occur in the same system. At low temperatures, chemisorption may be so slow that essentially only physisorption is observable, and at high temperatures physical adsorption can be insignificant compared to the chemisorption process [Steele, 1993] [Adamson and Gast, 1997]. Chemisorption and physisorption are generally distinguished based on the heat evolved during adsorption, which is small for physisorption (usually less than 20 kJ/mol) and larger for chemisorption (more than 200 kJ/mol) [Laider, 1987].

**Physisorption**

Physisorption is ubiquitous since all molecules and atoms will, to some extent, experience long range van der Waals forces, and all gasses below their critical temperature tend to adsorb as a result [Kolasinski, 2002] [Bruch et al., 2007]. The nature and relative size the interaction between adsorbed molecules and the surface (M-S interactions) and between molecules in the adsorbed layers (M-M interactions) determines the observed behavior of the system. During the adsorption process, thermodynamic equilibrium is obtained rapidly in comparison to chemisorption, and the physisorption process is always exothermic [Roquerol et al., 1999], [Steele, 1974]. The electronic perturbations that occur in physical adsorption are typically small, and both the adsorbed molecules and the adsorption substrate retain their original chemical identity after the molecules are desorbed [Bruch et al., 2007], [Roquerol et al., 1999].

Physisorption can be described in terms of short range repulsive and long range van der Waals attractive interactions. Repulsion arises from the overlap of atomic orbitals of the adsorbed molecules with electron states on the surface of the substrate.
The pair-wise Lennard-Jones potential is often used to describe the gas-solid potential curve:

\[ V_{LJ} = 4\epsilon_{g-s} \left[ \left( \frac{\sigma_{g-s}}{\rho_i} \right)^{12} - \left( \frac{\sigma_{g-s}}{\rho_i} \right)^6 \right] \]  

(2.1)

where \( \epsilon_{g-s} \) is the depth of the energy well and \( \sigma_{g-s} \) is the distance at which the interaction of the gas with an atom in the solid changes from positive to negative and \( \rho_i \) is the distance between the particles. The \( \rho_i^{-12} \) term represents short range repulsion, and the \( \rho_i^{-6} \) term describes the long range attractions of molecules.

**Chemisorption**

When molecules or atoms are chemically adsorbed onto a surface, both the adsorbate and the adsorbent may undergo large changes in their electronic structure [Steele, 1974]. The chemisorbed species tend to be localized at particular sites on the surface, and therefore only monolayers are significant in chemisorption since any molecules not in the monolayer cannot react with the significant surface sites [Ertl, 1987]. [Roquerol et al., 1999]. The process is also highly directional, like most bond formation processes, and the binding energy of a molecule can depend on its orientation with respect to the substrate [Kolasinski, 2002]. Unlike physisorption, which is always an exothermic process, the energy associated with chemisorption processes is comparable in both magnitude and sign to a chemical reaction, albeit generally exothermic as well [Roquerol et al., 1999]. The chemisorption process generally takes significantly longer to reach equilibrium than the physisorption process.

**2.2.2 Adsorption Isotherms**

In an adsorption isotherm, gas molecules are exposed to a surface in a closed system that is held at a fixed temperature \( T \) and allowed to come to equilibrium. The pressure of the gaseous phase decreases as molecules move from the (3D) gas phase to the 2D adsorbed phase. The system is allowed to come to thermodynamic equilibrium, so
the chemical potential of the 2D adsorbed phase \( \mu^{2D_{film}}(T) \) is equal to the chemical potential of the 3D gas phase \( \mu^{3D_{gas}}(T) \). Vertical risers appear in isotherm plots of the equilibrium pressure versus the amount of adsorbed gas, and this vertical region correspond to the majority of gas phase molecules that are introduced to the system move into the 2D phase, and the more horizontal regions correspond to an increased presence of molecules in the gas phase (i.e. the chemical potential is constant in the vertical region, and increases in the horizontal regions). As additional amounts of gas are added, the equilibrium pressure value increases. Eventually, enough gas is added to form a bulk phase. The pressure at which this occurs is the saturated vapor pressure, often designated as \( P_0 \).

**Isotherm Models**

There are several models that have been developed to describe isotherms. One of the earliest to be developed was by Irving Langmuir. The Langmuir isotherm is based on the idea of localized adsorption on energetically uniform adsorption sites. When the system is at equilibrium, the rate of desorption is equal to the rate of adsorption, and the equivalence of the rates of adsorption and desorption was used to kinetically derive the equations associated with this isotherm model. The rates are a function of the fraction of occupied surface sites. At low pressures, the fraction of sites occupied is a function of the gas pressure, and as pressure increases a monolayer forms. Inherent in this model is the assumption that the heat of adsorption has a constant value, regardless of the fraction of surface coverage. This is related to the assumption that neighboring molecules do not interact with each other [Wise and Oudar, 2001]. Langmuir’s model also assumes that only a single monolayer will be adsorbed onto a surface, and that all adsorption sites on the surface are equivalent. These are clearly nonphysical assumptions, but the Langmuir isotherm model has been used as a foundation for the development of more physical models.

The BET model, named for Brunauer, Emmett, and Teller, expands on the Langmuir model and allows for multiple layer formation [Brunauer et al., 1938].
This model also takes into account some intermolecular interaction, specifically the interaction of a molecule in a layer with molecules in an adjacent layer. However, this model does not incorporate for lateral interactions between molecules in the same layer [Wise and Oudar, 2001]. The BET model can be associated with five types of adsorption curves, shown in figure 2.6, along with a Type VI isotherm. These isotherm curves roughly describe the different types of adsorption that occurs when weaker or stronger physisorption takes place, or when capillary condensation occurs. The type II model, which corresponds to multilayer formation on a nonporous solid, is most similar to the isotherms that will be presented in the results section. The BET isotherm does not provide accurate descriptions of the low and high coverage portions of an isotherm, and tends to underestimate adsorption at low coverages and overestimate it at higher coverages [Gregg, 1986] [Adamson and Gast, 1997]. The BET model is widely used today, especially for the adsorption of nitrogen at 77 K onto materials for the purpose of determining their surface area. The BET method for calculating the monolayer capacity provides fairly consistent values when applied over the equilibrium pressure range $0.05 < P/P_0 < 0.3$.

The type IV isotherm that is included in figure 2.6 shows the step-like formation of multiple layers. Isotherms of this type result from adsorption on very uniform and homogeneous surfaces. Two examples of this are the adsorption of methane and hydrogen on MgO(100). Methane forms a two dimensional layer that is in registry with the underlying MgO surface. The 2D film is such a good lattice match that the methane can form up to seven discrete layers on carefully prepared and handled MgO(100). Hydrogen films also exhibit multiple layers, and inter-layer transitions that can be observed in the isotherm data [Larese et al., 2006].

**Phases of Adsorbed Layers**

For many years, the study of 2D phases and phase transitions was not possible using isotherms because surface heterogeneity (a consequence of multiple exposed crystal faces on substrates) made it almost impossible. Surface films may exhibit the
Figure 2.6: Type I: A Langmuir type isotherm, coverage reaches one monolayer; Type II: Describes physical adsorption on a nonporous solid and includes multilayer formation; Type III: Occurs when adsorbate-adsorbent interaction is very weak. Types IV and V represent adsorption in pores where capillary condensation occurs and exhibit hysteresis upon desorption; Type VI represents the step-like formation of multiple layers [Gregg, 1986] [Adamson and Gast, 1997].
thermodynamic phase properties of solids, liquids, or vapors, just like the 3D analogs. Two dimensional phase changes can be detected using isothermal measurements, but these are generally only detectable for films adsorbed on substrates that are highly physically and chemically uniform [Roquerol et al., 1999]. As more uniform adsorbates have become available, isotherms have been more widely used to investigate phase behavior and changes. When phase transitions occur within an adsorbed 2D layer, they may be visible as a small substep in the adsorption isotherm, shown in figure 2.7 [Thomy et al., 1981]. Adsorbed 2D layers often undergo phase changes at different temperatures compared with those of the bulk adsorbates. For example, physisorbed layers on uniform surfaces generally follow the trends $T(2D)/T(3D) = 0.6$ and $T(2D)/T(3D) = 0.4$ for the melting and critical points, respectively [Thomy and Duval, 1994].

**Structure of Adsorbed Layers**

The microscopic structure of adsorbed layers may be in a configuration that is disordered and random, or incommensurate, or commensurate with respect to the substrate. Disordered layers do not exhibit any long range regular order within the layer. Incommensurate or nonregistered layers are formed such that the the molecules within the layer are organized in a regular array with long range order, but the layer order does not form a regular pattern related to the underlying substrate. These phases occur when the adsorbate-adsorbate interactions are dominant, with minimal contribution from the substrate interaction. Commensurate or registered layers also exhibit inter-layer order, and the inter-layer order can be mathematically related to the symmetry of the underlying substrate. These layer structures form when substrate-molecule interaction results in particles adsorbed in substrate potential minima. Some examples of the common relationships between adsorbed layers and surfaces are shown in figure 2.8. The structures of adsorbed layers can be studied with low energy electron diffraction (LEED), or X-ray and neutron diffraction of the
Figure 2.7: An example of phase changes in adsorbed films: xenon on graphite. The features in the isotherms are shown with the corresponding phase diagram. [Thomy et al., 1981]
adsorbed films. These techniques work best when the adsorbed layers are on uniform substrates with long range order.

**Wetting of Substrates**

The term ”wetting” is used to describe the evolution from 2D to 3D as surface coverage increases. For adsorption onto powders, this involves intergranular condensation as the pressure approaches the saturation pressure, $P_0$. Complete wetting describes a system where the film grows continuously from 2D to three dimensions. When incomplete wetting occurs, the 3D film does not grow continuously from the 2D film, but nucleates in droplets near surface defects. Systems may undergo a wetting transition, which is a change in the wetting behavior as temperature changes. This sometimes observed as a crossover from incomplete wetting to complete wetting as the temperature rises and approaches the 3D triple point [Thomy and Duval, 1994]. The wetting behavior of a system can be observed as a change in the shape of an isotherm as the pressure approaches $P_0$. When the adsorbate is wetting the system, the approach to the saturation pressure will be a smooth curve. This change in the saturation behavior is apparent in Thomy et al’s classic wetting study of ethylene on graphite and is shown in figure 2.9.

**Thermodynamics**

When volumetric adsorption isotherms are performed, the system is allowed to come to equilibrium after each gas addition. More specifically, the 2D and 3D systems coexist, hence any molecules in the surface phase are in equilibrium with those in the 3D (gaseous) phase. For two phases that are in equilibrium, the chemical potentials, temperatures, and pressures of the two phases are equal [Berry et al., 2002]. Equilibrium between a 2D and a 3D phase requires the chemical potential and temperatures must be the same, namely:

$$\mu^{3D_{gas}}(T) = \mu^{2D_{film}}(T) \quad (2.2)$$

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Figure 2.8: Common 2D commensurate surface layers on face-centered cubic planes. The larger circles represent adsorbed gas molecules and the black dots represent the order of the underlying surface. [Kolasinski, 2002]
Figure 2.9: Example of a wetting transition: ethylene on graphite. Isotherms are show for three temperatures: (1) 77 K (2) 90 K (3) 105 K. As the temperature increases, the system transitions from incomplete to complete wetting, which can be observed in slope as the isotherm approaches the saturated vapor pressure. [Thomy and Duval, 1994]
The chemical potential for an ideal gas may be calculated with respect to the saturated vapor pressure as:

\[ \mu - \mu_0 = k_B T \ln(P/P_0) \]  

(2.3)

The Clausius-Clapeyron equation relates the Gibbs free energy of two phases in equilibrium for a pure component. Larher developed a form of this equation that relates the temperature and pressure to the differential enthalpy and entropy and the heat of adsorption of the 2D adsorbed layer [Larher, 1992] [Larher, 1967] [Thomy et al., 1981]:

\[ \ln(P) = B^{(n)} - A^{(n)} \frac{T}{T} \]  

(2.4)

where \( B^{(n)} \) and \( A^{(n)} \) are the y-intercept and slope of the \( n \)-th layer. This formula can be used to calculate the differential enthalpy and entropy. These are calculated with respect to a standard state. The saturated vapor pressure (SVP) is selected as a standard state. At the saturated vapor pressure, the bulk form of the adsorbent at that temperature is being formed, and the number of layers of adsorbed gas is assumed to be infinite \( (n \rightarrow \infty) \). The pressure values associated with a given layer and temperature are determined by taking the numerical derivative of the isotherm and identifying the pressure value associated with the maximum in the derivative. The slope and intercepts of these layers can then be used to calculate the differential entropy \( (\Delta S) \), enthalpy \( (\Delta H) \), and the heat of adsorption \( (Q_{ads}^{(n)}) \) using:

\[ \Delta H = -R(A^{(n)} - A^{(\infty)}) \]  

(2.5)

\[ \Delta S = -R(B^{(n)} - B^{(\infty)}) \]  

(2.6)

\[ Q_{ads}^{(n)} = R(A^{(n)}) \]  

(2.7)
(\(\Delta H\)) and (\(\Delta S\)) should approach zero as coverage approaches the bulk reference state, while the \(Q_{\text{ads}}^{(s)}\) should also approach the heat of adsorption calculated at the saturated vapor pressure.

**Isosteric Heat of Adsorption**

The isosteric heat of adsorption, \(q_{st}\), is determined by the change in the pressure of the gas phase following an increase in temperature at constant surface coverage. The equation, which can be derived from the Clausius-Clapeyron equation is:

\[
q_{st} = RT^2 \frac{\delta \ln(p)}{\delta T} \bigg|_{\theta} \approx RT^2 \frac{\Delta(\ln(p))}{\Delta T} \tag{2.8}
\]

This heat of adsorption is coverage dependent and can be attributed to molecular interactions. Variations in the heat of adsorption with increasing coverage can result from interactions between adsorbed molecules, phase changes, or heterogeneity of the adsorption surface [Adamson and Gast, 1997]. Heterogeneity of the surface can lead to molecules preferentially adsorbing on the more energetically favorable sites first, and subsequently on less preferable sites [Everett, 1957].

Experimental determinations of the isosteric heats are not always reliable, especially at lower equilibrium pressures. The results are very sensitive to any error in the measurement, hence lower pressures and surface coverages do not necessarily yield accurate results, but accuracy does increase with increasing coverage [Roquerol et al., 1999]. At higher coverages, lateral interactions between neighboring adsorbed molecules increase, and \(q_{st}\), which is strongly influenced by lateral interactions, becomes more reliable [Kolasinski, 2002]. The isosteric heat is expected to increase as surface coverage approaches monolayer completion and the number of molecules in the layer, and therefore the amount of lateral interaction is greater, and then decrease sharply at the monolayer completion point. A more steady decrease in the isosteric heat after monolayer completion can be an indication of surface heterogeneity [Adamson and Gast, 1997] [Everett, 1957]. As the equilibrium pressure \(P_f\) approaches
the saturated vapor pressure, $P_0$, the heat of adsorption is expected to approach the bulk heat of formation of the adsorbed material [Adamson and Gast, 1997].

### 2.2.3 Hydrogen Adsorption

Hydrogen adsorbed onto a surface may act similarly to free hydrogen, it may dissociate into hydrogen atoms, or it may remain as molecular hydrogen, but engage in significant electron transfer with the surface. Hydrogen dissociation is common when adsorbed on metal surfaces, and the separation of the hydrogen molecule into hydrogen atoms occurs at a distance of about 0.5 Å from the metal surface. The hydrogen atoms then chemisorb to the metal surface. The dissociation of the hydrogen molecule begins with the $1\sigma$ and $2\sigma^*$ orbitals broadening as the molecule approaches the surface. The metal surface can then donate electron density to the $2\sigma^*$ antibonding orbital of the hydrogen molecule (see figure 2.10), a process known as back donation. This weakens the H–H bond and strengthens the H-metal interaction, and finally results in dissociation once enough electron density has been transferred to the $\text{H}_2$ molecule [Kolasinski, 2002]. This electron transfer can be detected as an increase in the work function of the metal [Conrad et al., 1974].

![Figure 2.10: Molecular orbitals of the hydrogen molecule](image)

Figure 2.10: Molecular orbitals of the hydrogen molecule
Chemically adsorbed molecular hydrogen was not observed until 1984, when Kubas et al discovered an intact hydrogen molecule attached to a metal ligand complex. This process involves the donation of electron density from the hydrogen molecule to the metal center to form a two electron, three center bond. The H–H bonds that are observed in these complexes are extended longer than those in free hydrogen (free H\(_2\) bond length 0.74 Å) by 20% to distances of 0.89 Å. This extension of the bond length corresponds to the donation of electrons by the hydrogen molecule - in the case where hydrogen has completely lost or donated an electron to form H\(^+\)_2, the bond length of the molecule is extended to 1.06 Å. Kubas characterizes H–H lengths of 0.8 to 1.0 Å as corresponding to chemically bonded H\(_2\), 1.0 to 1.6 Å indicates intermediate structures, and H–H distances of greater than 1.6 Å belong to compounds where the hydrogen has dissociated into chemisorbed atoms (see figure 2.11).

![Diagram](image)

**Figure 2.11:** Hydrogen-Hydrogen- metal configurations and the corresponding inter-hydrogen distances [Kubas, 2007]

Hydrogen-surface interaction can hinder the rotational potential of the hydrogen. A simple example of this is presented based on the potential of a H\(_2\) molecule in a hindered potential that has been modeled by [Olsen et al., 2011] and [Xu et al., 2009]. The potential that they use was developed for hydrogen molecules contained in carbon slit pores and in C\(_{60}\), respectively. This potential modifies the Lennard-Jones
potential to take into account the amount of electron density that resides between the two hydrogen atoms. The interactions between the confined hydrogen molecule and the carbon atoms of the fullerene were assumed to be pairwise additive. The interaction of the H\textsubscript{2} molecule with carbon atoms was treated as the sum of two H–C carbon interactions, each described by the standard L-J potential.

\[
V_{LJ} = 4\epsilon_{H-C} \left[ \left( \frac{\sigma_{H-C}}{r} \right)^{12} - \left( \frac{\sigma_{H-C}}{r} \right)^{6} \right]
\] (2.9)

Treating the potential as the sum of these two interactions, they modeled the hydrogen atom as a dumbbell with no electron density between the two H atoms. The authors addressed this by adding a third term to the potential sum, which they refer to as the three-site H\textsubscript{2}-C potential model. The third term was the Lennard Jones potential multiplied by a weighting factor \(w\). Using \(w\) allows for the shape of the hydrogen seen by the surface to be altered to reflect the anisotropy of the interaction potential.

\[
V_{H2-C} = V_{LJ}(r_1) + V_{LJ}(r_2) + wV_{LJ}(r_m)
\] (2.10)

where \(r_1\) and \(r_2\) are the distances of the two H atoms to a C atom and \(r_m\) is the distance between the midpoint of the H–H bond and the carbon atom. The adjustable parameters are then \(\epsilon_{H-C}\), the well depth of the H–C potential; \(\sigma_{H-C}\), which is related to the equilibrium distance as \(r_e = 2^{1/6} \sigma_{H-C}\); and \(w\), the weighting factor. Xu et al optimized these parameters, and obtained values of \(\epsilon_{H-C} = 0.371\) meV, \(\sigma_{H-C} = 2.95\) Å, and \(w=7.5\). To simulate a change in the electron distribution between the two hydrogen atoms, the weight factor \(w\) is varied from 0 to 15. The depth of the well increases as more electron density is shifted away from the individual hydrogen atoms and spread out between them. Increasing the electron density that is delocalized from the individual H atoms increases the depth of the potential well, indicating greater H-surface interaction.
Figure 2.12: Modified Lennard-Jones potential for H$_2$-C interaction. The weighting value $w$ that distributes electron density between the hydrogen atoms was varied, all other values were kept constant. Weighting $w = 0$ corresponds to dumbbell-like H$_2$, where there is no distribution of density between the two atoms, increasing values correspond to increasing electron density [Xu et al., 2009]
**Para and Ortho Hydrogen**

Quantum mechanical restrictions on the symmetry of the rotational wavefunction of molecular hydrogen produce two different spin isomers of H$_2$, those with even values of the rotational quantum number $J$ and those with odd values of $J$. Even values of $J$, i.e. 2, 4, and zero, correspond to antisymmetric wavefunctions where the only allowed rotational states are antiparallel ($\uparrow\downarrow$) and is the para state of hydrogen ($p$–H$_2$). Odd values of $J$, $J = 1, 3, 5...$ correspond to rotational states that are parallel ($\uparrow\uparrow$), the ortho state ($o$–H$_2$). The states have a degeneracy of $2J + 1$. Below 20 K, only the lowest rotational states ($J = 0, J = 1$) are thermally populated and need to be considered [Silvera, 1980] [Souers, 1979]. Conversion between the ortho state and the para state is forbidden for isolated or non interacting molecules. Interconversion can occur between the para and ortho states for collections of interacting hydrogen molecules, caused by the interaction between magnetic dipole moments of neighbors. In the low density gas phase, conversion can be very slow. The nuclear moment of a neutron can also cause a transition in the rotational state [Silvera, 1980]. The population ratios of $p$–H$_2$ and $o$–H$_2$ vary with temperature. At room temperatures, there is a 3:1 ratio of the ortho:para states, and this is referred to as ”normal hydrogen”, or $n$–H$_2$. Hydrogen that is predominantly in the para state can be prepared by cooling liquid hydrogen to 20 K and allowing the molecules to thermally equilibrate, which will result in 99.8 % para-H$_2$. The time for the hydrogen to reach thermal equilibrium may be several weeks. A faster method to reach this state involves exposing the hydrogen to a paramagnetic salt, such as ferric oxide or nickel decorated silica gel, at temperatures near 20 K. This paramagnetic conversion process takes minutes instead of weeks.

In the preceding section, a hindered rotational potential was briefly discussed with a simple interaction model. Now that the para and ortho state of hydrogen have been introduced, the interaction the rotational potential with a surface can be revisited. The $J = 1$ state of hydrogen has a three-fold degeneracy, and the three rotational
wavefunctions associated with these degenerate levels can be modeled with spherical harmonics, noting that the $z$ direction is along the molecular axis of the H$_2$ molecule:

\begin{align*}
\Phi_{p_z}(\theta, \phi) &= \frac{3}{\sqrt{4\pi}} \cos \theta \\
\Phi_{p_x}(\theta, \phi) &= \frac{3}{\sqrt{4\pi}} \sin \theta \cos \phi \\
\Phi_{p_y}(\theta, \phi) &= \frac{3}{\sqrt{4\pi}} \sin \theta \sin \phi
\end{align*}

(2.11)

(2.12)

(2.13)

The absolute value of the squared spherical harmonics for the $s$ state corresponding to the $J = 0$ rotational configuration, and the $p_x, p_y, p_z$ states are shown in figure 2.12. It can be seen that the $p_x$ (2.12c) and $p_y$ (2.12d) states are clearly positioned with respect to a surface in the x-y plane such they have more interaction with that surface than the $p_z$ (2.13b) state will, so the potentials for the $p$ states will split, and $p_x, p_y$ will have a deeper potential than $p_z$.

**Hydrogen on ZnO**

Previous investigations of the adsorption of hydrogen on ZnO has divide the behavior into three categories, referred to as Types I, II, III [Howard and Braid, 1984]. Type I occurs at room temperature and involves the rapid and reversible dissociation of hydrogen, which then forms Zn–H and O–H surface species. This adsorption/dissociation process participates in catalytic reactions. Type I is associated with the polar faces of ZnO. Type II is slow and irreversible at room temperatures, and also involves the dissociation of hydrogen, and the possible bridging of the hydrogen atoms across Zn and O atoms [Strunk et al., 2009]. This type is associated with the nonpolar faces of ZnO. These processes take place simultaneously [Fubini et al., 1982]. Type III adsorption occurs at low temperatures (77 K), where the hydrogen is molecularly and reversibly absorbed [Chang et al., 1973].
Figure 2.12: Spherical harmonics representing the $J = 0$ and $J = 1$ rotational states. The x-y plane can be thought of as a substrate for an adsorbed hydrogen molecule.
Palladium and Hydrogen

The interaction of palladium and hydrogen has been of interest for many years [Worsham et al., 1957], [Lynch and Flanagan, 1973], [Jobic et al., 1985], [Albers et al., 2004]. Hydrogen chemisorbs and dissociates on many different metals, but the hydrogen-palladium system also involves significant diffusion of hydrogen into the bulk palladium metal lattice to form PdH. The high solubility of hydrogen in palladium metal is a result of the interaction between the hydrogen 1s orbital and the 4d orbitals of palladium metal. The relative energy levels of these orbitals result in a covalent interaction between the hydrogen and palladium. The degree of covalency between hydrogen and palladium is much greater than hydrogen and other metals such as nickel or platinum. The degree of covalency and the extent of hydrogen solubility are directly related; likewise a greater electronegativity difference between hydrogen and a metal results in less hydrogen solubility [Messmer et al., 1977].

The extent of hydrogen diffusion into the palladium lattice is very large- the ratio of H:Pd can be as high as 0.7 under certain conditions! This process begins when hydrogen is first chemisorbed onto the surface of the palladium. At high enough temperatures and pressures the chemisorbed hydrogen atoms diffuse into the bulk FCC lattice of the palladium and occupies the octahedral interstitial positions [Lynch and Flanagan, 1973]. Two phases of PdH are formed, and the ratio of the phases depends on the amount of hydrogen in the lattice see figure 2.13. The α phase forms at low hydrogen concentrations and has a lattice constant of 3.89 Å; close to that of regular palladium metal. At high hydrogen concentrations, a β phase forms, in concert with an expansion of the palladium lattice to 4.02 Å. The two phases can coexist at intermediate hydrogen concentrations [Worsham et al., 1957]; the ratio of the phases is both pressure and temperature dependent [Jewell and Davis, 2006]. Diffusion of hydrogen into the palladium lattice is significant at room temperatures, but is believed to be very slow at temperatures near or below 60 K [Mitsui et al., 540] [Lynch and Flanagan, 1973] [Behm et al., 1983]. Characterizing the interactions
between palladium and hydrogen can be challenging because multiple processes appear to occur simultaneously: adsorption onto the metal surface, and absorption into the interior of the metal lattice. Complicating factors also include chemical and mechanical pre-treatment and sample history which also have a significant impact on the formation of a Pd-H phase. Worsham et al found that exposure to dry air, compared to argon exposure, after heat treatment significantly increased hydrogen adsorption [Worsham et al., 1957]. This is because the retention of hydrogen in bulk palladium metal is strongly influenced by trap sites and impurities [Mitchell et al., 2005]. Despite these challenges, some heats of adsorption for chemisorbed hydrogen on palladium have been reported on the order of 100 kJ/mol [Conrad et al., 1974] [Lynch and Flanagan, 1973].

2.3 Neutron Scattering

Neutron scattering is not traditionally considered a surface technique, since neutrons deeply penetrate matter unlike traditional surface probes such as LEED and XPS. However, neutrons can be employed for investigating surface adsorption phenomena if the materials used have a high surface to volume ratio. Neutron scattering is particularly useful for characterizing the dynamics and structure of hydrogen or hydrogen containing compounds because hydrogen has a large incoherent neutron scattering cross section and deuterium has a significant coherent scattering cross section. Other techniques, such as X-ray diffraction or infrared spectroscopy, can be very insensitive to the presence of hydrogen [Souers, 1979]. Neutron scattering is also a versatile technique that can be used to investigate both the structure and dynamics of materials. The neutron scattering results presented here will focus on the use of inelastic neutron scattering (INS) to probe the interactions between hydrogen molecules and substrate surfaces. The rotational transition of H₂ is readily observable with inelastic neutron scattering [Mitchell et al., 2005].
Figure 2.13: Figure (a) shows hydrogen atoms occupying the interstitial positions in a palladium lattice [Worsham et al., 1957]. Figure (b) is the phase diagram of $\alpha$ and $\beta$ PdH as a function of temperature and pressure [Jewell and Davis, 2006].
2.3.1 Inelastic Neutron Scattering

At low temperatures the position and lineshape of the $J(0 \rightarrow 1)$ rotational transition for dihydrogen can be used to provide information about the strength of the interaction between the hydrogen and the adsorption site [Mitchell et al., 2005]. The position of this transition is determined by the difference in the energy levels for the two rotational states. Earlier investigations have shown that the molecules in bulk solid hydrogen acts as 3D rotors, even at very low temperatures. The rotational energy for a 3-D rotor is given by:

$$E_J = BJ(J + 1) \quad (2.14)$$

Where $B$ is the rotational constant of the molecule, and is 7.35 meV for H$_2$. The rotational motion of adsorbed hydrogen that interacts strongly with a surface may be hindered and not act as a free 3D rotor, but as a 2D rotor instead. The energy of a 2-D rotor is given by:

$$E_J = BJ^2 \quad (2.15)$$

The energy change associated with transitioning from $J = 0$ to $J = 1$ is then $\Delta E_{P\rightarrow O} = 2B$ for a three dimensional rotor and $\Delta E_{P\rightarrow O} = B$ for a two dimensional rotor [Silvera, 1980]. The behavior of a hindered molecule can be seen in the adsorption of hydrogen on MgO - hydrogen that is adsorbed close to the surface, within the first or second layer, exhibits a $P\rightarrow O$ transition at 11.25 meV. This value is less than $2B$, and greater than $B$, and indicates that the hydrogen molecules are interacting strongly enough with the MgO to somewhat hinder their rotation, and they are in a football-like configuration that is intermediate between a 2D rotor and a 3D rotor. If the H$_2$ coverage is increased above three layers, some molecules do not interact as strongly with the MgO surface, so another peak at 14.7 meV ($2B$) appears in the spectrum corresponding to 3D rotor-like hydrogen [Larese et al., 2006].
Figure 2.14: The INS response of H$_2$ on MgO at several different coverages. At low coverages, the P $\rightarrow$ O transition is located at 11.25 meV, which indicates that the hydrogen molecules close to the MgO surface have taken on some planar character due to their interaction with the surface. As more molecules are added farther away from the surface, they act as bulk hydrogen, and the free-rotor line at 14.7 meV becomes visible [Larese et al., 2006].
The width of the $P\rightarrow O$ peak can also provide information about the binding between hydrogen and a surface. An increase in the width of the energy transfer range of the peak can indicate multiple adsorption sites that have slightly different energies. This broadened peak can be considered to be a superposition of several $P\rightarrow O$ transition peaks which, because the different adsorption sites have slightly different binding interactions (and therefore different ) with the adsorbed hydrogen molecules, occur at energies that are a little lower or higher than 14.7 meV. This behavior can be observed in a comparison of para-hydrogen molecules adsorbed onto graphite and carbon nanohorns. Both materials interact weakly with hydrogen, and have peaks centered at 14.7 meV. However, graphite offers uniform adsorption sites, while carbon nanohorns (and similar materials such as carbon nanotubes) do not [Jiang and Sandler, 2003] [Wilson et al., 2002]. Nanohorns offer multiple adsorption sites, such as the interior of the horns, the interstitial space between nanohorns, and the ridges and grooves on the exterior of the nanohorn clusters [Talapatra and Migone, 2002] [Fernandez-Alonso et al., 2007] [Wilson et al., 2002]. The effect of these multiple adsorption sites is that the $P\rightarrow O$ peak is significantly broadened and the peak intensity is lower compared to the response on graphite. There are at least three different adsorption sites on carbon nanohorns (the availability of some sites, such as the inside of the horns, depends on the chemical pre-treatment of the material), which all have slightly different binding energies associated with them, so the broadened peak shown in figure 2.15 might consist of the superposition of at least three different $P\rightarrow O$ transition peak energies. Arrows have been added to this figure to suggest the possible individual peak locations.
Figure 2.15: (a) INS response of H$_2$ on graphite and on carbon nanohorns (CNH) [J.Z. Larese, private communication]. Both peaks are centered at the 14.7 meV position. The peak for CNHs is broadened, and less intense at its maximum, because CNHs have multiple adsorption sites with slightly different binding energies. Arrows have been added to suggest the positions of the peaks that are superposed to form the broadened peak (positions have not been confirmed). (b) Image of nanohorns, which cluster together in “Dahlia” configurations, and an image of the tips of nanohorns. There are several possible binding sites on nanohorns.
Chapter 3

Experimental Details

3.1 Materials

3.1.1 Metal Oxides

High purity MgO and ZnO powders were prepared using a patented vapor phase method which bypasses a molten metal state [Kunnemann and Larese, 2001]. This method avoids the safety concerns associated with liquid metals and also allows for a high degree of control over the powder size, size distribution, and if applicable, morphology. The liquidus metal phase is avoided by heating metals in the presence of carbon to form a metal carbide, which is then heated to a higher temperature. When the temperature of the metal carbide is greater that the boiling point of the metal used, the metal carbide decomposes, releasing metal vapor. This method is appropriate for metals that form unstable metal carbides, and is especially well suited to the production of MgO since magnesium carbides (Mg$_2$C and the more stable Mg$_2$C$_3$) are thermally unstable and highly reactive ([Fjellvag and P., 1992], [Rueggberg, 1943]). Zinc carbide is also unstable at ambient conditions, which allows for the synthesis of ZnO [Shulzhenko et al., 2000]. Another advantage of this method is that metals that form stable metal carbides remain gettered in the graphite crucible, further purifying the metal oxide. Electron spin resonance spectroscopy performed on
MgO powders generated using this method shows only a small amount of manganese impurities (∼ 5 ppm), and none of the other metal impurities (including chromium, cobalt, and iron) that can be found in commercially available MgO powders (see figure 3.1).

The process begins with high purity metal samples (Mg ingot, Alfa Aesar, 99.9%, Zn rod, Alfa Aesar, 99.99+%%) which are cut into small pieces (1/4 cubes of MgO, ZnO circular slices that are 0.5 in diameter and 1/8-1/16 thick). They are then sonicated in acetone to remove any oils deposited during the cutting process, and washed in HCl and water to remove the outer oxide layer and thoroughly rinsed with deionized water and dried. The cleaned metal is layered in a graphite crucible with chunks of high purity graphite. The crucible is topped with a layer of graphite chunks, such that no metal cubes easily visible. Based on the typical masses of metal and graphite chunks placed in the crucible, the molar ratio of Mg to C is 1:5 and the molar ratio of Zn to C is 1:10. The crucible is placed inside the coils of a radio frequency inductance furnace and a glass chimney, topped with baffles and a vent, surrounds the apparatus. Ultra high purity (UHP) argon gas is flowed through the system to purge out any atmospheric gasses prior to the start of the reaction. Argon gas also flows throughout the reaction, serving as a carrier gas to transport the metal vapor, and also assisting with heat transfer throughout the system. The crucible is heated to a temperature that should be near the melting point of the metal, and is allowed to dwell there for several minutes. The temperature is then increased to a temperature that should be near the boiling temperature of the metal. It has been observed that for the highest quality MgO, as determined by CH$_4$ on MgO isotherms, the ramping from the initial temperature to a higher temperature needs to occur before, or shortly after, significant softening/melting of the MgO cubes occurs, which can be observed when the graphite ”rocks” on top of the crucible sink to a lower level. The higher second temperature decomposes the metal carbide and releases metal vapor, which is visible as wisps of smoke rising from the crucible. At this time, oxygen gas is flowed into the halo above the crucible, and allowed to continue flowing until the reaction
Figure 3.1: Electron spin resonance spectroscopy of MgO powders prepared using patented Kunnemann-Larese method. This shows only a small amount of manganese impurities in the MgO powders. [J.Z. Larese, private communication]
is completed. The MgO powders are collected and stored under argon until they are used. Several different batch compositions of ZnO can be produced by varying the reaction conditions, such as the flow rates of argon and oxygen, the rate at which the material is heated, and the temperature that it is heated to. Figure 3.2 shows images of several different ZnO samples that were synthesized with the process outlined here. Small changes in reaction conditions can result in significant changes in the metal oxide product, and obtaining ZnO powders that have consistent morphology throughout is a challenge and an ongoing area of investigation.

**MgO Sample Quality**

The quality of MgO is evaluated with methane on MgO adsorption isotherms. Methane layers adsorbed onto MgO match well with the underlying MgO lattice. This substrate-adsorbate lattice match means that methane can form several well ordered layers on MgO, up to seven can be observed by taking the numerical derivative of the isotherm [Larese, 1998] [Larese et al., 2009] [Freitag and Larese, 2000]. High quality MgO samples will have minimal terracing on the edges of the cubes, and a high surface-to-volume ratio, e.g. large cubes. Poor quality samples will have a lot of terracing and this results in many edge effects. The isotherms (figure 3.4) and images (3.3) shown are comparisons of high and low quality MgO. The high quality MgO isotherm shows several key features that indicate a good sample. The second step in the isotherm is vertical, and is at least 70% of the height of the first step in the isotherm. Several steps can also be easily observed. A poor quality sample will have a second step with a riser that is sloped instead of vertical, and is a small fraction of the height of the first step. There are also fewer observable steps in the isotherm. MgO samples of moderate quality, but not the highest possible quality, were used for metal decoration.
Figure 3.2: ZnO structures synthesized using the methods described here
Figure 3.3: Figure (a) shows a good batch of MgO, which exhibits minimum terracing at the edges and corners of the cubes. Figure (b) shows poor quality MgO, with extreme surface terracing and a wide variation in the size of the MgO cubes.

ZnO Sample Quality

ZnO sample quality was evaluated with a combination of photoluminescence, imaging, and X-ray diffraction. Photoluminescent spectra was used to assess consistency between different batches of ZnO. The determination of what constituted a "good" batch was based on comparisons of SEM images and photoluminescent spectra during initial investigations into reaction parameters. Zinc oxide batches with the photoluminescence spectra of a "good" batch correlated with the presence of at least some tetrapods, whereas ZnO that has broad visible peaks shifted to higher wavelengths correlated with more hexagonal pillars and plates. Subsequently photoluminescence spectroscopy was primarily used to characterize batches of ZnO, since the fluorometer was more readily accessible than electron microscopy instrumentation.

The photoluminescence observed for the ZnO synthesized here varies from much of what is observed in the literature. Generally, the visible peak is centered at higher
Figure 3.4: Methane isotherms of high quality and poor quality MgO.
wavelengths, (Umar et al., 2005), (Dai et al., 2002), (Vanheusden et al., 1995), associated with the frequently discussed green emission band. The good batches of ZnO (figure 3.5) displayed a visible peak centered at 440 nm, and a smaller peak in the shoulder of this peak at 482 nm. The visible peak had a greater peak intensity than the UV peak at 380 nm. This small peak on the larger visible peak has not been observed in any of the reviewed literature for photoluminescence of ZnO. It should be noted that this peak is present, in the same location, in all batches that have been evaluated, including poor quality batches or batches that have undergone high temperature heat treatment. This suggests that this peak may not have to do with a surface defect, but perhaps a defect within the lattice. The wavelength of this peak is still within the range of wavelengths that are associated with oxygen vacancies or zinc interstitials, and does not seem to be associated with the presence of other chemical impurities. Poor quality batches of ZnO generally showed a decrease in the intensity of the visible peak and a shift in the center of the peak towards higher wavelengths, although some batches would show a greatly enhanced visible peak intensity, which was still shifted to higher wavelengths (figure 3.6).

X-ray diffraction was measured on the ZnO powders. The results, shown in figure 3.7, indicate that the ZnO is crystalline and has the bulk wurtzite structure. The diffraction profile did not show any peaks associated with the presence of metallic zinc. Tetrapods and nanorods that are synthesized in the gas phase show the (101) peak as most intense, followed by (100), then (002), which is consistent with preferential c-axis growth [Wu et al., 2005], [Dai et al., 2002], [Umar et al., 2005]. These results are consistent with the diffraction measured on the ZnO powders used here, where the relative intensities of the peaks (101), (100) and (102) are 1.00, 0.64, and 0.41, respectively.

An SEM of the specific sample of ZnO that was used for hydrogen and methane adsorption work is shown in figure 3.8. This image shows the mixed morphology nature of the sample. Tetrapods and needles are significant, but vary in composition. There are also a low concentration of hexagonal pillars and plates that are visible.
Figure 3.5: Photoluminescent spectra of several batches of ZnO that would be considered acceptable to use in adsorption work or for metal decoration.
Figure 3.6: Photoluminescent spectra of several batches of ZnO that would not be used for further experiment. The black curve corresponds to a reference sample of good ZnO.
Figure 3.7: X-ray diffraction of ZnO powders. The results indicate the wurtzite phase ZnO, and are consistent with X-ray diffraction of tetrapods and needles of ZnO.
Figure 3.8: SEM image of the ZnO sample used in the hydrogen and methane adsorption work presented here. The powder consists of a mixture of ZnO morphologies.
ZnO Heat Treatment

Under ambient atmospheric conditions, most metal oxides will chemisorb water to form surface hydroxyls, and may also physisorb water [Nagao, 1971], [Woll, 2007], [Henrich and Cox, 1994]. Adsorbed water and surface hydroxyls can be removed from metal oxide surfaces by heating the materials to high temperatures while they are being evacuated. In the case of ZnO, the extent and nature of the adsorption depends on the exposed surface. For example, studies have suggested that water adsorbed onto the nonpolar, energetically stable (10\bar{1}0) face remains in a molecular state, and begins desorbing at 370 K, with complete removal by 470 K, while the polar, oxygen terminated (000\bar{1}) face forms hydroxyls which are not removed until heat treatment temperatures exceed 800 K [Noei et al., 2008].

Photoluminescence studies were used to determine the heat treatment for the ZnO powders used in these experiments. The bulk melting and decomposition temperatures of ZnO are above 2000 K, but the PL spectra indicates that the defect concentrations are affected at much lower temperatures. Similar temperature dependent changes in PL spectra were reviewed by Singh and showed increasing defects as temperatures increased from 873 K to 1273 K [Singh, 2007]. Figure 3.9 shows the changes in the photoluminescence spectra of the synthesized ZnO upon heating. Heating the powder to 950°C under vacuum for 12 hours, which is similar to the treatment of MgO powders, lead to a significant increase in the magnitude of the visible peak, as well as a shift to higher wavelengths. As reviewed in section 2.1.2, the visible peak is attributed to defect concentrations, hence this treatment appears to have drastically increased the defect concentration. The spectra collected after heat treatment at 250°C under vacuum for 12 hours does not vary significantly from the untreated photoluminescent spectra, and there is even a slight decrease in the magnitude of the visible peak.

These results are consistent with literature cited in [Anpo and Che, 2000], where the sharp UV peak was not affected by heat treatment, but the visible emission peak
Figure 3.9: Photoluminescent spectra of ZnO prior to any heat treatment, after heat treatment at 250°C, and at 950°C for 12 hours while being evacuated.
center shifted to longer wavelengths. Based on the PL spectra, a heat treatment temperature of 250° was selected, and samples were heated at this temperature while being evacuated (base pressure $5 \times 10^{-7}$ torr) for a minimum of 12 hours. This heat treatment appears to remove any hydroxyls which may be present on the surface of the ZnO. INS collected on the ZnO samples at LANSCE and ISIS show no observable hydroxyl stretches [J.Z. Larese, private communication].

### 3.1.2 Metal Decoration of Metal Oxides

#### Choice of Deposition Method

We now turn to a discussion of the method that was selected for the deposition of metal clusters onto metal oxide supports. It was important to select a method that would allow for deposition of the clusters with minimal destruction of the metal oxide supports. Commonly used methods for metal deposition, such as palladium chloride dissolved in HCl, were not favorable because ZnO is easily etched by acids [Henrich and Cox, 1994] [Ozgur et al., 2005] [Burton et al., 2008]. A solvent that would have a minimal effect on the morphology and surface of the ZnO nanostructures and could be easily removed was preferable. Acetone has been selected as a solvent in other palladium deposition studies specifically because it does not destroy ZnO morphology the way that acids do [Burton et al., 2008]. ZnO is certainly sensitive to the presence of acetone, and has been studied for use as an acetone sensor, but that may not necessarily indicate that acetone reacts chemically with the ZnO surface under the conditions here. Acetone will chemically react on ZnO when the ZnO is heated in air at temperatures above 250° C [Sahay, 2005]. Acetone has not shown reactivity on the oxygen face of ZnO, and desorbs as an intact molecule. The zinc face also desorbs intact acetone molecules over the temperature range 25-470°C [Vohs and Barteau, 1991].

There have been some investigations into the adsorption of acetone onto MgO. Most of these studies were investigating catalytic activity, and MgO was selected
because it is a prototypical structure, even though catalytic activity on bulk MgO is much lower than on other basic solids [Sanz et al., 1999] [Oveido and Fernández Sanz, 1998]. A problematic aspect of these studies is that several of them refer to MgO and Mg(OH)₂ interchangeably [Miyata et al., 1974], [Lercher et al., 1981]. This distinction is important because impurities in MgO, including hydroxyls, as well as other impurities such as CaO, K, Fe, and Na increase the catalytic activity of MgO [Zhang et al., 1988], [Tanabe et al., 1989], [Lercher et al., 1981]. Edges and defects also increase the reactivity of MgO, which is consistent with studies over the past 20 years that have established that the coordination numbers of surface Mg and O affect hydrogen adsorption and desorption [Kakkar et al., 2006]. Infrared studies on MgO samples, which do not clearly distinguish between MgO and Mg(OH)₂, generally indicate that acetone will adsorb onto the Mg site and the keto-enol tautomerism shifts to favor the enol form. As the temperature is elevated above 140°C, the peaks associated with the enolate complex disappears and new peaks appear, which are generally attributed to carboxylate or carbonyl compounds on the surface of the MgO.

An ab initio investigation of acetone on a perfect MgO(100) surface indicates that acetone and MgO interaction is mainly an electrostatic polarization of the acetone, and is therefore physisorbed, not chemisorbed. It is clear from this survey that the extent of interaction between the acetone solvent and the MgO is greatly dependent on the quality of the MgO(100). The MgO used here is very chemically pure and free of hydroxyls prior to the metal decoration process, so the reactivity with acetone should be low.

**Palladium on ZnO**

The correct amount of palladium acetate was calculated to give 1% by weight palladium metal on ZnO. The molar mass of trimeric palladium (II) acetate is 673.52 g. A sample calculation of palladium acetate mass is shown:
For 10 g ZnO, 1% Pd metal by mass is 0.1 g

\[
0.1g \text{Pd metal} \times \frac{1 \text{mole Pd}}{106.42g \text{Pd}} \times \frac{1 \text{mole Pd Acetate}}{3 \text{moles Pd}} \times \frac{673.52g \text{Pd Acetate}}{1 \text{ mol Pd Acetate}} = 0.211g \text{Pd Acetate}
\]

The correct amount of palladium acetate (Strem Chemicals, 98%) was weighted and placed in a 250 ml round-bottom flask with an egg shaped \(\frac{1}{2}\)” x 1” Teflon coated stirring bar. Approximately 50 mL of HPLC acetone (Fisher Scientific, 99.5%) was added to the flask and the contents were stirred until the palladium acetate crystals dissolved. The ZnO powder was then added while stirring, and additional acetone was added as needed to allow for a homogeneous slurry to form. The mixture was stirred vigorously at a rate of speed that was fast enough to prevent the formation of separate layers in the flask (see figure 3.9). A rubber septum sealed the flask and a nitrogen gas line and a vent needle were inserted in the septum. The mixture was stirred continuously under a flow of nitrogen until the solvent was evaporated and a fine powder remained. This process took less than six hours, and the resulting product was a peachy-yellow color.

This powder was then placed in a quartz boat, which was placed into a glass flow apparatus. This apparatus was placed in a furnace and a mix of 4%H\(_2\)/balance UHP argon gas was flowed over the sample. The sample was heated at 200°C under flowing gas for 12 hours to reduce the palladium metal. After reduction, the powder was a dark grey color. The flow furnace configuration is shown in figure 3.11.

When large amounts of material were needed for neutron scattering experiments, the material was mixed with bare ZnO powder, which served as a filler. The final treatment of the samples prior to loading them into adsorption cells or neutron cans was to heat treat them under vacuum for a minimum of 12 hours at 200°C until they reached a base pressure of \(5 \times 10^{-7}\) torr according to an in-line ion gauge. The large amounts of material used in neutron cells (35 g) usually required longer heat treatment times to reach this base pressure, but not exceeding 48 hours.
Figure 3.9: Pictures of the metal decoration process. Figure A shows the palladium acetate dissolved in acetone. The palladium acetate should be completely dissolved before adding the ZnO. Figure B shows the slurry that is formed after the addition of the ZnO powder. Figure C shows what can happen if the stirring speed is not rapid enough: palladium will be deposited on the walls of the flask as the solvent evaporates. Figure D shows the mixture being stirred and with the nitrogen line and the venting needle inserted.
Figure 3.10: Palladium decorated ZnO powders loaded into a quartz boat before reduction (Figure A, yellow powder) and after reduction with 4% H$_2$ gas/balance UHP argon gas at 200$^\circ$C for 12 hours.
Figure 3.11: Flow furnace set-up for reducing metal decorated metal oxide powders. The glass flow tube is shown encased in the furnace. Inside the flow tube is a quartz boat containing grey powder. The valves that can be used to isolate the contents of the flow tube are represented by circles with Xs inside.

Imaging of Palladium on ZnO

A close up of the palladium clusters on ZnO is shown in figure 3.12, which shows the palladium particle wetting the ZnO surface. The palladium metal clusters appear to be polycrystalline and are probably the product of smaller particle agglomeration. Figure 3.13 is a wider view that shows the metal clusters dispersed on the legs of a ZnO tetrapod. The clusters appear to be 5-10 nm in diameter and there are some oblong shaped clusters that appear to have been formed by two or more smaller clusters.

XPS of Palladium on ZnO

X-ray photoelectron spectroscopy (XPS) was used to evaluate the metal decorated powders. The instrument used to do this was a Thermo K-Alpha X-ray photoelectron spectrometer. The spectra were collected on the powder samples after they had been briefly evacuated (less than 10 minutes) at room temperature. It should be noted that the powders were exposed to atmosphere before they were loaded, and the evacuation time and temperature would not be sufficient to remove surface adsorbates. These include CO$_2$, which leads to the "ubiquitous" or "adventitious" carbon peak around
Figure 3.12: Close up TEM image of palladium decorated ZnO powders. Images taken by David Cullen.
Figure 3.13: Close up TEM image of palladium decorated ZnO powders. Images taken by David Cullen.
285 eV, and is found on all samples that have been exposed to the atmosphere [Vinek et al., 1978].

The Pd/ZnO powders were characterized with XPS, and the Zn 2p, Pd 3d, C 1s and O 1s peaks are shown in figure 3.13. The zinc peak position is in agreement with the expected position for ZnO, 1021.5 eV [Mulligan et al., 2003]. The palladium 3d peaks are located at 334.7 eV (3d_{5/2}) and 340.0 eV (3d_{3/2}), which are the expected positions for Pd^0. If the palladium was present as Pd^{2+}, the peaks would be expected to shift to 336.9 eV and 342.3 eV, respectively. This indicates that the palladium clusters were completely reduced to metallic palladium [Cubeiro and Fierro, 1998] [Iwasa et al., 1995]. As noted above, the carbon spectra shows the ubiquitous carbon peak at 284.6 eV, and also a smaller peak at 288.4 eV, which may indicate the presence of additional carbon compounds on the surface of the material, which may have been deposited during the metal decoration process. The oxygen spectra consists of large peak at 530.0 eV, which corresponds to the lattice oxygen atoms, and a smaller, broad peak located at about 533 eV. This peak is usually associated with surface hydroxyls, although it could also consist of contributions from the presence of oxygen atoms in the residual carbon compounds that were indicated by the C 1s peak [Cubeiro and Fierro, 1998].

**Gold on ZnO**

Gold was also deposited on ZnO using the same general procedure and acetone solvent as was described for the decoration of palladium on ZnO. Hydrogen tetrachloroaurate hydrate (Aldrich, 99.999%), abbreviated as HTCA in the equation below, was used to introduce the gold. A sample calculation is shown for 1% gold (0.1 g) on 10 g of ZnO:

\[
0.1 g \text{ Au metal} \times \frac{1 \text{ mole Au}}{196.97 g \text{ Au}} \times \frac{1 \text{ mole HTCA}}{1 \text{ mole Au}} \times \frac{393.833 g \text{ HTCA}}{1 \text{ mol HTCA}} = 0.20 g \text{ HTCA}
\] (3.2)
Figure 3.13: XPS for Pd decorated ZnO materials.
The gold decorated ZnO powders were a pale yellow-grey prior to reduction. The powder turned purple after reduction, which is consistent with gold nanoparticles varying from red to blue in color depending on their size. These powders were treated the same way described for the palladium decorated ZnO prior to loading in adsorption cells or neutron cans.

**Imaging of Gold on ZnO**

High resolution TEM images of gold decorated ZnO are displayed in figures 3.14 and 3.15. The gold clusters on the ZnO appear to be 2-4 nm in diameter, with some larger 5 nm clusters as well. The gold clusters appear as though they may not wet the metal oxide support surface as well as the palladium clusters in ZnO and MgO, which could indicate a weaker interaction of the gold with the ZnO.

**XPS of Gold on ZnO**

XPS spectra were collected on the gold decorated ZnO powders. The Zn 2p peak was located at the expected position of 1021.4 eV for ZnO [Cubeiro and Fierro, 1998]. The gold peaks overlaps with the Zn 3d peak, so it is more difficult to provide an accurate representation of the electronic state of the gold clusters. The results have been deconvoluted into peaks that show the presence of both metallic gold and Au$^{3+}$, although the reliability of the results is limited by the peak overlap. The carbon spectra shows the ubiquitous carbon peak, and a small shoulder that could also indicate the presence of other carbon compounds on the surface. This peak is much smaller (using the intensity of the ubiquitous peak as a standard) than the carbon peak observed on the Pd/ZnO sample. The oxygen spectra consists of a peak at 530.5 eV that is from the lattice oxygen, as well as the shoulder that can be attributed to surface hydroxyls and possibly oxygen contained in carbon compounds.
Figure 3.14: Close up TEM image of gold decorated ZnO powders. Images taken by David Cullen.
Figure 3.15: Wider view TEM image of gold decorated ZnO powders. Images taken by David Cullen.
Figure 3.15: XPS for Au decorated ZnO materials.
Palladium on MgO

When working with MgO, it is important to minimize air and water exposure. The water that is present as either physisorbed molecules or that may be surface hydroxyls (a result of this exposure) can be removed by heating the MgO to 950°C in vacuo. Once the MgO has been decorated with metal, exposing the materials to high temperatures would encourage metal cluster aggregation. The procedure described below was designed to minimize surface hydroxylation while avoiding high temperature treatments after metal cluster deposition.

The MgO was prepared for metal deposition by first heat treating the bare material, as previously described, to 950°C under vacuum for 36 hours. Following this heat treatment, the MgO was handled in a UHP argon environment.

The necessary mass of palladium acetate was weighted and then placed in a round-bottom flask with a stir bar. The round-bottom flask, a new bottle of HPLC acetone and the heat treated MgO, still sealed in a quartz tube, were placed in a glovebag. The glovebag was flushed with argon three times, the HPLC acetone was opened and the void space in the bottle was flushed with argon, and then the entire bag was flushed two additional times. Acetone was added to the round bottom flask, and the acetone and palladium acetate were stirred until the palladium acetate was dissolved. The MgO powder was added to the flask and a septum was inserted into the top of the flask. The flask was then removed from the glovebag, and a positive pressure of argon was introduced through the septum, with a needle for argon venting. The mixture was stirred vigorously until the acetone solvent was evaporated and a fine pale yellow powder remained. The flask was then brought back into a glovebag, along with a quartz boat and glass flow apparatus (see fig 3.11). The Pd decorated MgO was transferred from the flask to the quartz boat, and the boat is then placed in the flow reactor. The reactor was sealed off and removed from the glovebag. It was then placed in a furnace and 4%H₂/balance UHP argon gas was flowed over the sample during the metal reduction process. The sample was heated at 200°C for
12 hours to reduce the palladium metal. This change in the state of the palladium metal was readily observed as the powder changed from a pale yellow to a dark grey color. The flow reactor was then brought back into an argon filled glovebag and the metal decorated MgO was sealed inside of a quartz tube. The sample remained under argon in the quartz tube until final heat treatment and transfer to an adsorption cell or neutron scattering cell. The final heat treatment consisted of evacuating the quartz tube containing the material and heat treating it under vacuum at 200 °C for at least 12 hours and until they reached a base pressure of \(5 \times 10^{-7}\) according to an in-line ion gauge. The large amounts of material used in neutron cells usually required longer heat treatment times to reach this base pressure, but not exceeding 48 hours.

**Imaging of Palladium on MgO**

The first set of images, fig 3.15, shown here is a compilation of SEM images of the MgO before and after decoration. They show that the degree of terracing of the MgO is not dramatically different after the metal decoration process. MgO corners are usually rounded after prolonged exposure to atmosphere, and these rounded edges likely form many terraces once the sample undergoes heat treatment at 950 °C for 36 hours under vacuum. The powders did not undergo this treatment after metal deposition, so any etched and rounded corners would be visible. Figure 3.16 is a high resolution TEM image that is a close up of the palladium clusters on the MgO. The half-circle shape of the metal clusters indicates that they seem to wet the MgO surface, which could promote metal-support interaction. The clusters appear polycrystalline, which may be a consequence of smaller particles sintering together. The wider field image gives a better view of the particle sized. They appear to be between about 5 nm in diameter, with some larger 10 nm clusters as well.
Figure 3.15: MgO before and after metal deposition. Figures (a) and (b) are SEMs of MgO that has been heat treated. Figures (c) and (d) are MgO that has been decorated with palladium clusters. These images are not high resolution, so the metal clusters are not highly visible. The MgO appears to exhibit a similar degree of terracing before and after treatment, and there is no visible rounding of the corners that occurs upon exposure to water vapor. Images taken by Craig Bridges.
Figure 3.16: Close up TEM image of palladium decorated MgO powders. Images taken by David Cullen.
Figure 3.17: Wider field TEM image of palladium decorated MgO powders. The metal clusters appear to have an average diameter of about 5 nm. Images taken by David Cullen.
**XPS of Palladium on MgO**

XPS data was collected on the Pd/MgO powders. The Mg peak is located at the expected position for MgO, 49.7 eV. The palladium 3d$_{5/2}$ peak overlaps with the Mg Auger peak, but the 3d$_{3/2}$ peak position is more visible, at 341 eV, which is within the range of values assigned to metallic palladium. The carbon spectra shows a peak at 288.5 eV in addition to the ubiquitous carbon peak, which once again may indicate the presence of carbon compounds that were deposited during metal decoration. The most dramatic feature may be the oxygen peak— the peak from lattice oxygen is present at 530 eV, but a second peak of equal intensity is also present at 532.2 eV. This peak position is indicative of surface hydroxyls or oxygen from carbon compounds. This massive peak indicates that the MgO surface was negatively affected by the metal decoration process. This was confirmed when INS indicated a small concentration of hydroxyl stretches on the material prior to the introduction of any gasses, e.g. when the background was collected on the material.

### 3.1.3 Thermodynamic Experiments

**Monolayer Completion and Surface Area**

The amount of gas that is adsorbed onto the surface during an isotherm (moles adsorbed) can be calculated using the ideal gas law, with an appropriate correction for the presence of gas molecules which do not adsorb to the surface. Gas molecules that are introduced into the adsorption apparatus can either adsorb to the surface, or remain in the coexisting gas phase and not be adsorbed. Therefore the total number of moles of gas that have been introduced to the sample cell, $n_{total}$ is equal to $n_{ads}$ plus $n_{not-adsorbed}$. Rearranging this equation:

$$n_{ads} = n_{total} - n_{not-adsorbed}$$ (3.3)
Figure 3.17: XPS for Pd decorated MgO materials.
The total number of moles introduced for any gas addition, $n_{total}$, can be calculated using the initial pressure, $P_i$, in the calibrated volume portion, $V_{calibrated}$ of the isotherm apparatus. The moles of gas that are not adsorbed, $n_{not-adsorbed}$ may reside either in the sample volume or the calibrated volume. Inserting this into the equation $n = \frac{PV}{RT}$ gives:

$$n_{ads} = \frac{P_i \cdot V_{calibrated}}{RT_{298\,K}} - \left( \frac{P_f \cdot V_{calibrated}}{RT_{298\,K}} + \frac{P_f \cdot V_{sample}}{RT_{sample}} \right)$$  

(3.4)

When this equation is generalized for multiple additions of gas, the resulting formula for moles adsorbed is:

$$n_{ads} = \frac{\Sigma \Delta P \cdot V_{calibrated}}{RT_{298\,K}} - \frac{P_f \cdot V_{sample}}{RT_{sample}}$$  

(3.5)

[Thomy et al., 1981]

The number of moles that corresponds to a monolayer of coverage was calculated using a modified point B method. The point B method defines a point, which corresponds to monolayer completion, as the point at the beginning of the nearly linear region of the isotherm. For a BET isotherm, this value is frequently obtained by fitting a line to the linear region from $0.05 < \frac{P}{P_0} < 0.3$. Monolayer determination using the point B method yield values that give fairly constant surface area values, and also correspond well to the point where there is sharp decrease in the isosteric heat [Gregg and Sing, 1982]. A modified point B method has been used to calculate monolayer coverages here which involved fitting two straight lines, one corresponding to the vertical riser in the isotherm and the other over a range corresponding to the nearly horizontal region that follows the monolayer knee. The intersection of these two lines is taken as the monolayer coverage value, as shown in figure 3.18. For adsorption on bare ZnO powders, the linear fit region could not be extended out to $\frac{P}{P_0} < 0.3$ because of the presence of another feature in the isotherm. A linear fit was obtained over the range $0.05 < \frac{P}{P_0} < 0.25$. The metal decorated metal oxides show a
broad knee in the monolayer completion region, and the most suitable range to fit a line to was \(0.1 < \frac{P}{P_0} < 0.3\).

**MgO Surface Area**

Methane isotherms can also be used to calculate the surface area of MgO samples. Diffraction studies ([Larese, 1998]) show the area that a methane molecule will occupy on MgO. The number of moles of methane present at monolayer completion are calculated using a modified point B method that fits intersecting lines to the vertical and horizontal portions of the first step. The number of moles that correspond to the intersection point are multiplied by 17.72 Å\(^2\) to give the surface area of the MgO powder (see figure 3.19). The MgO powders used for metal decoration had a surface area of approximately 10 m\(^2\)/g prior to metal deposition.

**ZnO Surface Area**

Unlike methane adsorbed on MgO, there is no diffraction data available for methane or hydrogen on ZnO that can be used to precisely determine the surface area of our ZnO powders. This means that an assumption must be made about the area that the molecule will adsorb on the surface. There can be some variability in what this value might actually be- molecules might follow a simple hexagonal packing on the surface, but in some systems, the molecular area may be larger or smaller if the molecules have preferred adsorption sites or a preferred orientation on the surface. This is seen for hydrogen on MgO, which actually packs more densely on the surface than it does in bulk hydrogen ([Larese et al., 2008]), and adsorbate area per molecule (APM) for nitrogen may vary from 11.2 to 20 Å\(^2\) per molecule, depending on the surface. In an attempt to get a general sense of what the ZnO surface area is, several methods were used to calculate the surface area using multiple sets of empirical data and assuming different surface configurations of adsorbed (hydrogen and methane) molecules:
Figure 3.18: Point B method for determining monolayer completion. This shows the method applied to a hydrogen on Pd/ZnO, over the range $0.1 < \frac{P}{P_0} < 0.3$. 
Figure 3.19: Methane molecule on MgO(100) [Larese, 1998]
(1) Diffraction data of the hexagonal close packed phase of bulk \( n \)-hydrogen (collected for temperatures 1.3 - 4 K) was used to calculate the area of a 2D projection of a hydrogen molecule in a hexagonal arrangement [Mills and Schuch, 1965]. This gives an APM of 12.25 Å\(^2\)/molecule.

(2) The same diffraction data can be used to calculate the area occupied by hydrogen in a square lattice, which gives an APM of 14.145 Å\(^2\)/molecule.

(3) Diffraction data from Bostanjoglo on solid hydrogen leads to slightly larger APMs - 12.34 Å\(^2\)/molecule for hexagonal packing,

(4) and 14.24 Å\(^2\)/molecule for a square lattice [Bostanjoglo and Kleinschmidt, 1967].

(5) Edler et al presented, not specific to adsorption on a specific surface, 14.4 Å\(^2\)/molecule as the APM for for liquid density packing of hydrogen,

(6) and 11.7 Å\(^2\)/molecule for solid hydrogen [Edler et al., 1997].

(7) Using the van der Waals constants for methane, an area per molecule of 18.1 Å\(^2\)/molecule was calculated. This was used in conjunction with methane isotherm monolayer coverages.

The surface area values presented here were obtained using an average of all of the monolayer capacities over the range of isotherm temperatures. The smallest proposed APM for hydrogen gives a surface area of 8.914 m\(^2\)/g, while the largest proposed value gives an APM of 10.997 m\(^2\)/g. The values calculated for hydrogen coverage give an approximate surface area of 10 m\(^2\)/g. However, the area calculated using a methane APM and the methane monolayer coverage, the surface area value is 5.01 m\(^2\)/g. This discrepancy is quite significant and may be a reflection of the gas molecules (either the hydrogen or methane) adsorbing to the surface in a packing configuration other than the ones used here.

Adsorption Isotherm Apparatus

A schematic of the adsorption isotherm apparatus is shown in figure 3.20. This gas handling system is equipped with both manually and electronically controlled
<table>
<thead>
<tr>
<th>Method Number</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>9.33 ± 0.12</td>
</tr>
<tr>
<td>(2)</td>
<td>10.80 ± 0.14</td>
</tr>
<tr>
<td>(3)</td>
<td>9.42 ± 0.12</td>
</tr>
<tr>
<td>(4)</td>
<td>10.85 ± 0.14</td>
</tr>
<tr>
<td>(5)</td>
<td>11.00 ± 0.14</td>
</tr>
<tr>
<td>(6)</td>
<td>8.91 ± 0.12</td>
</tr>
<tr>
<td>(7)-CH₄</td>
<td>5.01 ± 0.01</td>
</tr>
</tbody>
</table>
valves. The use of electronically controlled valves allows for isotherm experiments to be automated, which results in higher quality isotherms than what can be generated manually. A program generated within the Larese group ([Mursic et al., 1996]) using National Instruments LabVIEW controls four of the valves in the isotherm apparatus, which are referred to by number. Valve 1, which allows gas into the sample cell, is a Swagelok 6LVV-DPS4-C air actuated, electronically controlled diaphragm valve. While these valves are designed to have smaller leak rates and longer lifetimes than Swagelok B-4HK brass bellows valves, we have found these valves to be very sensitive to the presence of particulate, with small amounts of powder or debris causing large leaks. To extend the lifetime of valve 1, this valve was used as a one-way valve to introduce gas into the sample cell. Once an isotherm was completed, a bypass B-4HK valve was used to evaluate the sample. A result of this configuration is that Valve 1 is not located directly in front of the sample capillary. There is an additional volume in the "T" that is between Valve 1 and the sample cell capillary. In order to get accurate dead space corrections, the volume of this "T", which is at room temperature, needs to be incorporated into the equation for moles of gas adsorbed:

\[
    n_{ads} = \frac{\sum \Delta P \cdot V_{calibrated}}{RT_{298K}} - \left( \frac{P_f \cdot V_T}{RT_{298}} + \frac{P_f \cdot V_{sample}}{RT_{sample}} \right)
\]  

Valve 2, also a 6LVV-DPS4-C, allows gas from the gas reservoir into the dosing volume of the apparatus. Behind valve 2 is a Swagelok B-4BMG 10-turn valve which meters the gas and allows the gas pressure to slowly rise. Valves 3 and 4, which are Swagelok B-4HK valves, can be opened to expose the system to vacuum. Valve 3 has a metering valve behind it to allow for a gradual reduction of gas pressure. Valve 4, which is not used during the course of an isotherm, opens the system to vacuum without metering the gas. Additional valves shown in figure 3.20 allow for sections of the system to be isolated as needed. Pressure within the system is monitored using an MKS 690A12TRA model 100 torr capacitance manometer (torr head accuracy ±0.05% of reading), powered by an MKS 270B signal conditioner, equipped with
Figure 3.20: Schematic of isotherm station. The computer controlled valves are numbered and represented with colored circles. The black numbered valves correspond to Swagelok 6LVV-DPS4-C. The grey numbered valves correspond to Swagelok B-4HK valves outfitted with pneumatic actuators. The green circles correspond to B-4HK valves which are manually operated. The small white circles correspond to metering valves. The volume that is shaded light blue corresponds to the volume $V_{\text{calibrated}}$. The volume that is shaded light green corresponds to the volume $V_T$. The pink shaded volume corresponds to the volume $V_{\text{sample}}$. This schematic is not drawn to scale.
a digital pressure readout. The temperature of the sample is read and controlled using a Cryocon 32B temperature controller and two Lakeshore DT-670 silicon diode thermometers. One thermometer is mounted on the tip of the compressor cold finger and the other is mounted on top of the sample cell. The thermometer on the cold finger of a closed cycle helium refrigerator is the "control" thermometer, and its reading are used to determine the amount of heater output needed. The thermometer mounted on the sample cell is the "sample" thermometer, and the temperatures from this thermometer are used to determine the temperature of the sample cell.

Sample temperature is controlled with a closed system helium cryostat, a heater, and the previously described silicon diodes and a Cryocon temperature controller. An ARS 4 K expander (model DE-2025-G) and an ARS-4HW closed cycle helium compressor are used to cool the sample. The sample cell is mounted on the tip of the expander, with a small amount of vacuum grease used to improve thermal contact and two screws holding the edge of the sample cell and the stage of the expander in mechanical contact. A strip heater is applied to the top of the expander with Kapton tape, and the "control" thermometer is mounted a cm above the heater, held in place with vacuum grease and a washer and screw that screws into the expander tip. The sample thermometer is mounted to the top of the sample cell using vacuum grease and a brass screw and washer that screw into a threaded hole in the lid of the sample cell. The sample cell and the cold finger of the expander are surrounded by a vacuum shroud and a 77 K radiation shield to reduce thermal transfer from outside of the system. A feed-through on the aluminum ring attached to the sample cell connects the cell to the rest of the gas handling apparatus. After each isotherm, samples were warmed up and the adsorbed gas was evacuated through the bypass. Samples were evacuated for a minimum of 8 hours at room temperature prior to beginning another adsorption experiment.
Temperature Corrections Using the Vapor Pressure of Hydrogen

The saturated vapor pressure was used to calculate the temperature that the isotherm was performed at. Prior experimentally determined values of the vapor pressure vs. temperature of $n$-hydrogen were used for the temperature range of 10.12 K to 20.56 K [Woolley et al]. Below 10.12 K, the solid-gas equation formulated by Souers et al [Souers et al., 1977] was used:

$$\ln(P_{\text{solid-gas}}) = A + \frac{B}{T} + B'\ln(T)$$  \hspace{1cm} (3.7)

where, for normal hydrogen, $A$ is 2.678183 torr, $B$ is -86.94152 and $B'$ is 2.860678.

Figure 3.21 displays a plot of both the experimentally measured pressures and the calculated pressures. The calculated pressures were extended to a temperature of 13 K to establish the excellent agreement between the two data sets. In this overlap region the experimental values were used for the present isotherm studies temperature determinations.

Thermal Transpiration Corrections to Hydrogen Gas Pressures

At low pressures, the phenomenon of thermal transpiration, or thermomolecular flow, can be significant and needs to be taken into account. Thermal transpiration occurs when a gas is in two volumes at different temperatures that are connected by a small capillary. A thermal gradient will occur along the connecting capillary if the diameter of that capillary is close to or less than the mean free path of the gas molecules [Broom, 2008], [Roquerol et al., 1999]. If the tube diameter is much greater than the mean free path of a gas, the pressure will be the same throughout the system [O’ Hanlon, 1989]. Applying this information to the isotherm system shown in figure 3.20, this means that the pressure measured by the manometer may vary from the pressure that is in the lower temperature sample cell.

Knudsen published several papers describing the flow of gasses at low pressures, and established some parameters to assist in characterizing gaseous behavior (see
Figure 3.21: Hydrogen vapor pressures from 8 to 14 K. The red points correspond to pressures calculated using the solid-vapor equilibrium equation from [Souers et al., 1977]. The blue data points were empirically measured by Woolley et al. An overlap region is shown to demonstrate the consistency between the two sets of vapor pressures. The empirical data was used over the available temperature range, and the calculated values were used outside this range.
references in [Steckelmacher, 1986]). Two gaseous regions were defined, the Knudsen region and the molecular flow region. In the Knudsen region, molecule-wall collisions dominate over molecule-molecule collisions, therefore diffusion is assumed to be independent of the number of gas molecules. In the molecular diffusion region, molecule-molecule collisions provide resistance for the diffusion of a species, and therefore diffusion is affected by the number and type of gas molecules present. A transition region between these two regimes also exists where both molecule-molecule and molecule-wall interactions matter [Remick and Geankoplis, 1973]. The region that is applicable to a system can be assessed with the Knudsen number, $Kn$,

$$Kn = \frac{\lambda}{L}$$

(3.8)

where $\lambda$ is the mean free path of the molecule and $L$ is the capillary diameter. $Kn > 1$ is the free molecule threshold where the mean free path of the molecule exceeds the capillary diameter, the range of $0.01 < Kn < 10$ is attributed to the transition region, and $Kn < 0.01$ is the Knudsen, or continuum, regime. This is displayed graphically in figure 3.22. Table 3.2 shows values of the Knudsen number that were calculated for pressures and temperatures that were applicable to the experiments performed here. The inner diameter of the capillary used in this system was 0.9652 mm. The mean free path of hydrogen molecules was calculated using the simplest version of the kinetic theory of gases, which treats molecules as hard spheres of diameter $d$ participating in binary collisions. The mean free path was calculated as:

$$l = \frac{kT}{\pi\sqrt{2P}d^2}$$

(3.9)

where the diameter of a hydrogen molecule is $d = 2.71 \times 10^{-10}$ m [CRC handbook]. The results displayed in this table indicate that thermal transpiration corrections are appropriate for the hydrogen adsorption at low temperatures. Values are not
Figure 3.22: Knudsen values over a range of capillary diameters and molecular mean free paths [Broom, 2008]
displayed for pressures that exceed the saturated vapor pressures for the specified temperatures.

Knudsen proposed that, in the region defined by $Kn < 0.01$, the pressure gradient can be described as

$$\frac{P_2}{P_1} = \left( \frac{T_2}{T_1} \right)^{\frac{1}{2}} \quad (3.10)$$

where $P_2$ and $T_2$ are the pressure and temperature of the sample, and $P_1$ and $T_1$ are the pressure and temperature of the system where the manometer is located. Several empirically based equations have been proposed to address the pressure gradient that occurs in the transitional range between molecular and Knudsen flows. Takaishi and Sensui proposed equations to describe the behavior of gasses in this regime, which were based on their empirical measurements of several gases. The equation that they designate 4' is most applicable to the isotherm system described here because it applies to systems where one of the connected volumes is held at a temperature lower than room temperature ($T_1 < T_2$):

$$\frac{P_1}{P_2} = \frac{AX^2 + BX + C\sqrt{X} + \sqrt{\frac{T_1}{T_2}}}{AX^2 + BX + C\sqrt{X} + 1} \quad (3.11)$$

Where $A = A^*\bar{T}^{-2}$; $B = B^*\bar{T}^{-1}$; $C = C^*\bar{T}^{-\frac{1}{2}}$; and $\bar{T} = \frac{T_1 + T_2}{2}$, and $A^*, B^*, C^*$ are constants. The constants are assigned a temperature range 14 - 673 K. Much of the data here is at temperatures lower that the 14 K lower limit temperature, but these parameters are the lowest temperature parameters available, and were therefore used on all data. Takaishi calculated constants for several different gasses, and indicated that the results for hydrogen, based on five different sets of data, are the most reliable. The pressure readings that have had the thermal transpiration correction are referred to here as $P'$. The corrected pressure applies to the pressure of the gas in the low temperature portion of the apparatus, so the equation for moles adsorbed (originally
**Table 3.2:** Knudsen Values for H$_2$ Over Applicable Temperature and Pressure Ranges

<table>
<thead>
<tr>
<th>P (Torr)</th>
<th>15 K</th>
<th>13 K</th>
<th>11 K</th>
<th>9 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.493</td>
<td>0.428</td>
<td>0.362</td>
<td>0.296</td>
</tr>
<tr>
<td>0.5</td>
<td>0.099</td>
<td>0.086</td>
<td>0.072</td>
<td>0.059</td>
</tr>
<tr>
<td>1.0</td>
<td>0.049</td>
<td>0.043</td>
<td>0.036</td>
<td>–</td>
</tr>
<tr>
<td>5.0</td>
<td>0.010</td>
<td>0.009</td>
<td>0.007</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>0.005</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>20</td>
<td>0.003</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
presented in equation 3.5) becomes:

\[
n_{ads} = \frac{\sum \Delta P \cdot V_{calibrated}}{RT_{298K}} - \left( \frac{P_f \cdot V_T}{RT_{298}} + \frac{P' \cdot V_{sample}}{RT_{sample}} \right)\quad (3.12)
\]

For plots of amount adsorbed versus pressure, the pressure used on abscissa is also the corrected \( P' \) value. Application of this thermal transpiration correction to isotherm data significantly alters the calculated \( \Delta H \) and \( \Delta S \) values. The results calculated after correcting the data exhibit the trends that would be expected as coverage increases towards bulk, while the uncorrected data did not.

### 3.1.4 Neutron Experiments

Samples were prepared for neutron experiments with the same heat treatments as described previously. The neutron cells used to contain the materials are described in [Koehler and Larese, 2000] and allow for the dosing of gas on the powders in situ. Large amount of powders were used in the neutron experiments so that significant responses could be measured from the adsorbed films. For bare powders, such as ZnO, approximately 10-15 grams of material would be used in a neutron cell. The exact amount of material was recorded at the time of cell filling. The metal decorated powders underwent significant compacting during the metal decoration process. They were mixed with undecorated powders to increase the volume that the powders occupied. Even with the blending of the powders, significantly more metal decorated material was used in neutron cans, usually on the order of 20-40 g decorated material mixed with 5-10 grams of undecorated material. The powders were heat treated as described previously to remove surface contaminants, particularly adsorbed water and other weakly bound species. Following heat treatments, the powders were loaded into sample cans in a UHP argon filled glovebox to retain the clean surfaces. The samples are stored under UHP argon for transportation to the neutron scientific facilities, and the argon gas was evacuated for at least 6 hours prior to the use of the samples in experiments.
In advance of the neutron experiments, the gas coverage properties of the powders were determined. For ZnO, this was done by running an isotherm on the actual sample in the neutron cell. A methane isotherm was performed on the material while the neutron sample can was immersed in liquid nitrogen. The relative capacity of methane to hydrogen adsorbed on ZnO had been measured, so the methane isotherm could be used to determine the hydrogen coverage. The relative coverages, shown in figure 3.23, are 3.1:1 for H₂:CH₄ at monolayer completion, and 1.9:1 for H₂:CH₄ for the hydrogen substep. The capacities of the metal decorated materials have only been measured at low temperatures. For these neutron samples a small aliquot of the exact same batch of material that was loaded into a neutron cell was reserved and used to fill a standard adsorption cell to perform hydrogen "calibration" isotherms. The neutron cell capacity was then determined by scaling up the mass of the sample. A gas handling system, like the isotherm station described here, was used at the neutron facility to dose the desired amounts of gas onto the powder samples.

For the neutron experiments shown here, the hydrogen gas was converted fully to the para state (using a paramagnetic salt as described in section 2.2.3) before dosing it onto the samples to ensure that the molecules are in the \( J = 0 \) rotational ground state. The neutron results shown here are difference scans. This technique is used because the small signal from the adsorbed film behavior is what is of primary interest. Difference scans are generated by first collecting data on the evacuated sample prior to the introduction of any gas (just the bare ZnO or Pd/ZnO, etc). Gas is then added and more data collected. When these two scans are subtracted from each other, the resulting data should only reflect signal from the adsorbed gas film [Mitchell et al., 2005].
Figure 3.23: Hydrogen and methane monolayers on a sample of the same mass. The substep on hydrogen is located at 1.9 times the monolayer capacity of methane adsorbed at 77 K. Hydrogen monolayer completion has a capacity of 3.1 times the capacity of methane.
Chapter 4

Results and Discussion

4.1 Hydrogen Adsorbed on ZnO

4.1.1 Features in the Hydrogen on ZnO Isotherm

Substeps and small features between layers in an adsorption isotherm can be used for identifying phase and layering transitions within the adsorbed layers (see [Dash, 2002], section 2.2.2). However, these transitions are most reliable when the adsorption substrate is chemically uniform and when single facet exposure is predominant, which is not the case here. The ZnO powders used in this study vary somewhat in morphology, and are likely to have multiple crystal faces exposed. Hence, the features that appear in the H\textsubscript{2} isotherms are likely due to the presence of different surface sites which have different adsorption energies associated with them. The hydrogen may preferentially adsorb on the most favorable sites first, and then adsorb to the less preferential sites at higher chemical potentials.

An issue that was encountered with hydrogen adsorption on all of the systems reviewed here, including ZnO, was the verticality of the monolayer riser. For gas adsorption at higher temperatures, such as methane adsorption at 77 K, the monolayer riser has a steep slope, but is not perfectly vertical. This non-verticality allows for the calculation of a numerical derivative to locate step positions, as was
discussed in section 2.2.2. The first risers of the hydrogen isotherms performed here, at temperatures below 14 K, were extremely vertical, most likely due to the strong binding of the hydrogen to the ZnO, hence the extremely low vapor pressure, which was below the resolving power of the pressure manometer and it was not possible to take numerical derivatives of these regions. This verticality is demonstrated in Figure 4.2, where the monolayer regions of a hydrogen and a methane isotherm are shown. For the hydrogen on ZnO system, the additional features that are present were analyzed using a Clausius-Clapeyron plot.

4.1.2 Adsorption Isotherms

Adsorption isotherms were performed over the temperature range of 8.97 to 13.7 K. Numerical derivatives revealed the presence of three features in the isotherms. An easy to discern substep (labeled Feature 1) can be seen in the monolayer completion region, and there are two additional and much smaller features (Features 2 and 3) at higher pressure. A representative isotherm of hydrogen is shown in figure 4.3, and a close-up of the features of this isotherm, as well as their numerical derivatives, are shown in figure 4.4. A compilation of all of the isotherms that were performed is in figure 4.5. The range of adsorption pressures, and the range of temperatures are demonstrated in this plot, but the finer details of these isotherms were displayed in the representative isotherm figure.

4.1.3 Clausius-Clapeyron Thermodynamics

Clausius-Clapeyron parameters were calculated for these features. Figure 4.6 shows the plot of these features with linear lines fit to them. The slope and intercept, $A$ and $B$, are listed in table 4.1, and the thermodynamic values that were calculated using the equations presented in section 2.2.2 are listed in table 4.2. Using these calculated quantities indicates that hydrogen is physically adsorbed on ZnO for the temperatures studied. This is consistent with the expected "Type III" adsorption
Figure 4.1: The monolayer capacity of hydrogen on ZnO appears to drop more drastically around 11 K.
Figure 4.2: The vertical risers of H$_2$ and CH$_4$ isotherms. The CH$_4$ isotherm is shown to accentuate the verticality of the H$_2$ isotherm. Note that the sample coverages are not scaled for monolayer capacity comparisons.
Figure 4.3: A representative isotherm of hydrogen on ZnO, $T = 9.161$ K.
Figure 4.4: Adsorption features and their numerical derivatives for hydrogen adsorbed on ZnO. Feature 1 occurs in the monolayer completion region and is quite distinctive, features 2 and 3 can be difficult to discern without the assistance of the numerical derivative.
Figure 4.5: All of the isotherms of hydrogen on ZnO, T = 8.97-13.7 K.
Figure 4.6: Clausius-Clapeyron Plot for H\textsubscript{2} on ZnO
behavior for hydrogen on ZnO at low temperatures, where the hydrogen is molecularly and reversibly adsorbed.

**Table 4.1:** Clausius-Clapeyron parameters for H$_2$–ZnO system.

<table>
<thead>
<tr>
<th>Feature</th>
<th>$A$ (Error ($A$))</th>
<th>$B$ (Error ($B$))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feature 1</td>
<td>167.85 (2.458)</td>
<td>11.561 (0.226)</td>
</tr>
<tr>
<td>Feature 2</td>
<td>123.19 (2.478)</td>
<td>10.767 (0.224)</td>
</tr>
<tr>
<td>Feature 3</td>
<td>126.62 (0.873)</td>
<td>11.908 (0.079)</td>
</tr>
<tr>
<td>S.V.P. (n=∞)</td>
<td>118.07 (0.567)</td>
<td>12.392 (0.052)</td>
</tr>
</tbody>
</table>

**Table 4.2:** Thermodynamic Quantities for H$_2$–ZnO system.

<table>
<thead>
<tr>
<th>Feature</th>
<th>$\Delta H$ (kJ/mol) Error</th>
<th>$\Delta S$ (J/K*mol) Error</th>
<th>$Q_{ads}$ (J/mol) Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feature 1</td>
<td>-0.414 (0.0210)</td>
<td>6.91 (1.93)</td>
<td>1396 (20.4)</td>
</tr>
<tr>
<td>Feature 2</td>
<td>-0.0426 (0.0211)</td>
<td>13.51 (1.91)</td>
<td>1024 (20.6)</td>
</tr>
<tr>
<td>Feature 3</td>
<td>-0.0711 (0.00866)</td>
<td>4.024 (0.787)</td>
<td>1053 (7.26)</td>
</tr>
<tr>
<td>S.V.P. (n=∞)</td>
<td>—</td>
<td>—</td>
<td>981.7 (4.71)</td>
</tr>
</tbody>
</table>

4.1.4 Isosteric Heat of Adsorption

Isosteric heat of adsorption plots, shown in figures 4.7-4.10, were calculated at several temperatures. Again, the verticality of the hydrogen monolayer riser limits the range over which these calculations may be performed. When the difference of vertical regions of the two isotherms are taken (see eq 2.8), the result is basically the noise of the two isotherms amplified. This region has been excluded from the isosteric heat plots, but the behavior in this region is most accurately described as oscillations with an average value close to 0 J/mol, but magnitudes that can be very large. Calculating accurate isosteric heats can be a challenge,(see section 2.2.2) so the primary value of the isosteric heats presented here are (1) self-consistent results (2) exhibiting general trends that reflect the adsorption behavior. The maximum magnitude of the $q_{st}$ peak maximum at monolayer completion, for example, may not represent a definite value of the heat at that point, but can indicate that a maximum heat value occurred at that coverage. The coverages associated with features 1,2, and 3 have been marked
on all of the isosteric heat plots. Feature 1, the substep feature, corresponds with a sharp rise in the isosteric heat, followed by a decrease as the monolayer is completed. Features 2 and 3 appear to have variations in the isosteric heat associated with their locations, which could broadly be described as a rise and fall of the heat in this region before the heats continue their approach to the bulk coverage value. The highest temperature isosteric heat shows a considerable broadening and blurring of the heats compared to the lower temperature heats. This could indicate that at these temperatures the behavior of the film is beginning to change due to the increased thermal energy available.

4.1.5 Inelastic Neutron Scattering

Inelastic neutron scattering for several coverages of hydrogen on ZnO were measured with the TOSCA indirect geometry spectrometer at ISIS (Rutherford-Appleton Lab, Oxfordshire, U.K.). This instrument has an energy range of 1-500 meV, and a resolution $\Delta E/E$ of 2%. A sample can was filled with 17.0 g of bare ZnO powder, and the response of adsorbed hydrogen was measured at the base temperature of the instrument cryostat, $\sim 14$ K. Figure 4.11 shows the inelastic scattering response of several coverages (0.25 to 1.6 monolayers) of hydrogen on ZnO. Additionally, a reference peak corresponding to hydrogen on graphite is included. At all coverages, hydrogen on ZnO has a $P\rightarrow O$ peak centered at 14.7 meV. This indicates that the hydrogen is acting as a 3D free rotor that is interacting weakly with the ZnO surface. However, the peak shown here occupies a greater space in energy transfer compared to the $H_2$ on graphite peak. This broadening could be a consequence of the multiple adsorption sites that are present on the ZnO powders. As was discussed in section 2.3.1, different adsorption sites will have slightly different binding energies associated with them. For ZnO, these different binding sites could be a result of the multi facet exposure of the powders that were used. Hydrogen may interact more or less strongly with these multiple sites, which results in different energy values associated with the
Figure 4.7: Isosteric heat of adsorption of H₂ on ZnO. Temperature T = 9.29 K and ΔT = 0.644 K. The dashed lines correspond to the coverages of the three features discussed in section 4.1.2.
Figure 4.8: Isosteric heat of adsorption of H$_2$ on ZnO. Temperature T = 10.92 K and ΔT= 0.47 K. The dashed lines correspond to the coverages of the three features discussed in section 4.1.2.
Figure 4.9: Isosteric heat of adsorption of H\textsubscript{2} on ZnO. Temperature T = 11.86 K and ΔT = 0.52 K. The dashed lines correspond to the coverages of the three features discussed in section 4.1.2.
Figure 4.10: Isosteric heat of adsorption of H$_2$ on ZnO. Temperature T = 12.36 K and $\Delta T = 0.47$ K. The dashed lines correspond to the coverages of the three features discussed in section 4.1.2.
P→O transition. The observed broadened peak would result from a superposition of the distribution of energies. Another feature observable in the INS response of this material is a broad wing at higher values of energy. This feature is attributed to hydrogen molecular recoil.

The thermodynamic quantities calculated using the Clausius-Clapeyron equation and neutron scattering studies indicate that, for the temperatures studied, hydrogen is molecularly and physically adsorbed on ZnO. While there are variations in the maximum in the isosteric heat of adsorption plots, even the highest maximum value, 3000 J/mol, is well within the range of heats associated with physisorption.

4.2 Hydrogen on Palladium Decorated ZnO

4.2.1 Adsorption Isotherms

Adsorption isotherms were performed over the temperature range of 9.22 K to 13.45 K. These isotherms consisted of a single monolayer feature which is shown in a representative isotherm in figure 4.13. Figure 4.14 displays all of the isotherms that were measured. These isotherms were used to calculate the monolayer coverage of hydrogen on palladium decorated ZnO as a function of temperature. Unlike the hydrogen monolayer capacity on bare ZnO, these values do not show a clear temperature dependent behavior(figure 4.27). The variation between the maximum and minimum value is about 7%, which is the same variation seen for H2/ZnO, but a definite trend is not apparent. The thermodynamics of these isotherms were calculated with isosteric heat plots (figures 4.15-4.33). The monolayer coverage is marked on these plots with a black dashed line. The lower temperature isosteric heats show a small heat increase at the monolayer coverage, and the heat then continues to increase as it moves towards the bulk value. The lower temperature isotherms had corresponding low pressure values, and isosteric heats are not very reliable in the low pressure regime, so isosteric heats alone might not be enough to identify different
Figure 4.11: The INS response of H$_2$ on ZnO at several different coverages, expressed as fractions of monolayer coverage. The H$_2$ on graphite peak is included as a reference. The H$_2$ peak on ZnO is centered at the 14.7 meV free rotor position, but the peak occupies a greater space in energy transfer, which indicates several adsorption sites with slightly different binding energies.
adsorption in the low pressure region. The higher temperature isosteric heats show
more typical behavior, with a rapid increase in heat as monolayer completion takes
place. A feature that all of the isosteric heats share is an additional rise and dip after
monolayer completion. This may indicate a change in the adsorption behavior after
monolayer completion, and complimentary INS data presented in the next section
provides further insight into this.

4.2.2 Inelastic Neutron Scattering

Inelastic neutron scattering data was collected for para-hydrogen on palladium
decorated ZnO. The powdered sample used in this experiment was composed of 21.29
g of Pd/ZnO, which was 0.97 % Pd by weight, with an additional 16.11 g of bare
ZnO blended with the metal decorated powder. The experiment was performed
at the same instrument used for hydrogen on bare ZnO, the TOSCA indirect
geometry spectrometer at ISIS. The data was collected at the base temperature of
the instrument cryostat, \( \sim 14 \text{ K} \). The hydrogen gas was converted to the para state
with the assistance of a paramagnetic salt before it was adsorbed onto the Pd/ZnO
powders.

The P\( \rightarrow \)O transition that is observed for one monolayer of hydrogen on Pd/ZnO is
dramatically shifted compared to hydrogen on bare ZnO. The peak for this transition
is located at 6.5 meV. The predicted value for the P\( \rightarrow \)O transition for 3D hydrogen
is 14.7 meV\( (2B) \), and is 7.35 meV \( (B) \) for hydrogen that is acting as a 2D rotor.
The additional shift of this peak beyond this value strongly suggests that not only is
the H\(_2\) molecule behaving as a planar rotor, but the bond length has also extended.
The formula for the rotational constant of the molecule can be used to calculate the
extended bond length, which is 78.7 pm, a 6.19% increase compared to a bond length
of 74.1 pm in a free hydrogen molecule.

\[
B = \frac{\hbar}{2\mu r^2} \quad (4.1)
\]
Figure 4.12: Monolayer capacities of $\text{H}_2$ on Pd/ZnO from 9.22 K to 13.45 K
Figure 4.13: Representative isotherm of hydrogen on palladium decorated ZnO, $T = 11.03$ K.
Figure 4.14: All of the isotherms of hydrogen on palladium decorated ZnO, $T = 9.2-13.4$ K.
Figure 4.15: Isosteric heat of adsorption of hydrogen on palladium decorated ZnO. Dashed line indicates monolayer completion coverage. Temperature $T = 9.79$ K and $\Delta T = 1.15$ K.
Figure 4.16: Isosteric heat of adsorption of hydrogen on palladium decorated ZnO. Dashed line indicates monolayer completion coverage. Temperature $T = 10.49$ K and $\Delta T = 1.44$ K.
Figure 4.17: Isothermic heat of adsorption of hydrogen on palladium decorated ZnO. Dashed line indicates monolayer completion coverage. Temperature $T = 11.41$ K and $\Delta T = 0.76$ K.
Figure 4.18: Isosteric heat of adsorption of hydrogen adsorbed on palladium decorated ZnO. Temperature $T = 13.01$ K and $\Delta T = 0.88$ K. The dashed line indicates one monolayer of coverage.
Where \( \mu \) is the reduced mass of the hydrogen molecule and \( r \) is the interatomic distance. The presence of only one peak, which is very sharp (FWHM = 1 meV), indicates that the molecular hydrogen is adsorbing to a single site, most likely the palladium metal site. If a significant number of the hydrogen molecules were also adsorbed onto the ZnO surface, one would expect additional INS peak to appear at 14.7 meV, as was observed on the bare ZnO. Also worth noting is that there are no strong indications that PdH is formed when the para-hydrogen is adsorbed onto the palladium decorated ZnO. Stretches associated with Pd-H would be observed at 70.1 meV (565 cm\(^{-1}\)) for \( \alpha \)-PdH and 59.6 meV (480 cm\(^{-1}\)) for \( \beta \)-PdH [Mitchell et al., 2005], and there is no evidence for that in figure 4.19. A broad wing is visible at higher energies which, as for \( \text{H}_2 \) on bare ZnO, is attributed to the recoil of hydrogen molecules. The ratio of palladium metal to hydrogen molecules, Pd/H\(_2\), is approximately one-to-one at monolayer completion, which indicated a large palladium capacity for hydrogen molecules. The data presented here suggests that para-hydrogen molecules may preferentially adsorb to palladium metal sites at coverages of approximately one monolayer. Furthermore, it appears that the interaction between the para-hydrogen and the palladium nanoparticles is strong enough to significantly hinder the rotation of hydrogen. The H–H bond length extension indicates that the hydrogen molecule donated some electron density to the site where it was absorbed (see section 2.2.3). A density functional theory simulation of hydrogen on a palladium cluster on ZnO (see figure 4.20) shows a similar result, where some of the hydrogen molecules undergo a bond length extension of 6%, and some other hydrogen molecules dissociate [E. Cruz-Silvia, J.Z. Larese, private communication].
Figure 4.19: INS response for 1 monolayer of hydrogen adsorbed onto Pd/ZnO. The P→O transition is located at 6.5 meV. This is a significant shift from the 3D rotor value of 14.7 meV, and is in fact shifted past the value for a 2D rotor, 7.35 meV. This indicates that the hydrogen is behaving as a 2D rotor, and has also undergone a bond length extension.
Figure 4.20: Density functional theory simulation for hydrogen molecules on Pd/ZnO. This simulation shows some molecules with extended H–H bond lengths (blue arrow) and some dissociated hydrogen atoms (red arrow) [E. Cruz-Silvia, J.Z. Larese, private communication].

4.3 Hydrogen on Gold Decorated ZnO

4.3.1 Adsorption Isotherms

Adsorption isotherms were performed over the temperature range of 8.95 - 14.0 K. Similar to the palladium decorated ZnO, these isotherms also only exhibit a monolayer formation, as seen in the representative isotherm presented in figure 4.22. The collection of isotherms over the entire temperature range are shown in figure 4.23. The monolayer coverage exhibits a temperature dependence, with the capacity of the monolayer decreasing by about 8% over the studied temperature range, shown in figure 4.21.

The isosteric heats of adsorption show a sharp rise before monolayer completion, then a gradual decline. These heats do not exhibit the multiple features seen in the palladium on ZnO isosteric heats. This might indicate that there is not a strong adsorption-site preference. The values of the isosteric heats of adsorption are well within the regime of physical, not chemical, adsorption. The adsorption of hydrogen on gold decorated ZnO is clearly different than the adsorption behavior on bare ZnO, but further studies using additional probes such as neutron scattering are necessary.
to determine more about the interaction. It is possible that the hydrogen interacts weakly with the Au/ZnO, and the loss of additional features in the adsorption isotherm is caused by surface heterogeneity that is a result of the metal decoration process.

4.4 Hydrogen on Palladium Decorated MgO

Adsorption isotherms were performed on palladium decorated MgO over the temperature range 8.4-12.19 K. These isotherms, like the other metal decorated materials, show only a monolayer coverage feature for the adsorption of hydrogen. A representative isotherm displays this in figure 4.28, and the series of isotherms is displayed in figure 4.29. The monolayer capacity of hydrogen on palladium decorated MgO is shown in figure 4.27 as a function of temperature. The monolayer capacity decreases by about 8% as the temperature increases from 8.4 K to 12.19 K.

Isosteric heats were also calculated at several temperatures for this system. The isosteric heats all display a sharp increase near monolayer completion, and then a gradual decrease as they approach the bulk heat. It should be noted that the shape of these isosteric heats are not the same as those for hydrogen adsorbed on palladium decorated ZnO. The Pd/ZnO system exhibited an additional rise and dip in the isosteric heat after monolayer completion. The isosteric heats for MgO do hint at a dip at coverages corresponding to about 2.5 monolayers. These changes in the isosteric heat for the two systems indicate that different palladium support materials (ZnO vs MgO) noticeably alter the observed behavior.

Adsorption Behavior Near the Saturated Vapor Pressure

A change in the adsorption behavior of hydrogen on palladium decorated MgO appears to occur in the temperature range of approximately 10.5 K to 11.5 K. This change in behavior is observable as the equilibrium pressure of the isotherm approaches the saturated vapor pressure. At lower temperatures, the change in
Figure 4.21: Temperature dependent monolayer coverages of hydrogen on gold decorated ZnO. The coverage decreases by about 8% over the range of 8.95 to 14 K.
Figure 4.22: Representative isotherm of hydrogen on gold decorated ZnO, $T = 12.47$ K.
Figure 4.23: All of the isotherms of hydrogen on gold decorated ZnO, $T = 8.95 - 14$ K.
Figure 4.24: Isosteric heat of adsorption of hydrogen on gold decorated ZnO. Temperature $T = 9.38 \, \text{K}$ and $\Delta T = 0.85 \, \text{K}$. The dashed line indicates one monolayer of coverage.
Figure 4.25: Isosteric heat of adsorption of hydrogen on gold decorated ZnO. Temperature $T = 10.37$ K and $\Delta T = 1.21$ K. The dashed line indicates one monolayer of coverage.
Figure 4.26: Isosteric heat of adsorption of hydrogen on gold decorated ZnO. Temperature $T = 13.64\, K$ and $\Delta T = 0.72\, K$. The dashed line indicates one monolayer of coverage.
Figure 4.27: Temperature dependence of the monolayer capacities of H$_2$ on Pd/MgO from 8.4 K to 12.19 K. There is about an 8% decrease in capacity over this temperature range.
Figure 4.28: Representative isotherm of hydrogen on palladium decorated MgO, $T = 10.52\, \text{K}$. 
Figure 4.29: All of the isotherms of hydrogen on palladium decorated MgO, $T = 8.4$-12.19 K.
Figure 4.30: Isosteric heat of adsorption of hydrogen on palladium decorated MgO. Temperature $T = 8.48$ K and $\Delta T = 0.09$ K. The dashed line indicates one monolayer of coverage.
Figure 4.31: Isosteric heat of adsorption of hydrogen on palladium decorated MgO. Temperature $T = 9.98$ K and $\Delta T = 0.84$ K. The dashed line indicates one monolayer of coverage.
Figure 4.32: Isosteric heat of adsorption of hydrogen on palladium decorated MgO. Temperature $T = 11.43 \, \text{K}$ and $\Delta T = 0.46 \, \text{K}$. The dashed line indicates one monolayer of coverage.
Figure 4.33: Isosteric heat of adsorption of hydrogen on palladium decorated MgO. Temperature $T = 11.92\,\text{K}$ and $\Delta T = 0.527\,\text{K}$. The dashed line indicates one monolayer of coverage.
pressure appears to correspond to the "wetting" condition described in section 2.2.2, and identified by the continuous and smooth approach to the saturated vapor pressure. As the temperature increases, the change in pressure in this region is no longer a smooth transition to saturation, but is more discontinuous near the saturated vapor pressure, which is traditionally associated with incomplete wetting behavior. Figure 4.34 shows all of the isotherms of hydrogen on palladium decorated MgO, with the pressures scaled so that all of the saturated vapor pressure regions are observable and are not overlapping. Figure 4.35 shows the region of interest for the temperatures that correspond with a change in adsorption behavior. These results may indicate a change in the behavior of the 2D film on the Pd/MgO as the temperature increases. For traditional wetting on well defined substrates, most observed changes in wetting behavior involve an incomplete to complete wetting transition as temperatures increase [Dash, 2002], which is not the behavior observed here.
Figure 4.34: $H_2$ on Pd/MgO isotherms over the temperature range 8.43 K - 11.5 K. The equilibrium pressures were scaled to allow for the saturated vapor pressures to be observable for all isotherms.
Figure 4.35: The saturated vapor pressure regions for H$_2$ on Pd/MgO isotherms at 9.56 K, 10.56 K, 11.48 K, 11.75 K. The pressure on these plots is presented as $P/P_0$. Note that the approach to the saturated vapor pressure is smooth and gradual for the isotherm at 9.56 K, and becomes much more abrupt as the temperature is increased.
Chapter 5

Conclusions

In the work presented here, metal oxide powders were synthesized, and decorated with catalytically active metal clusters. The bare and metal decorated materials were characterized using electron microscopy, X-ray diffraction, photoluminescence, and X-ray photoelectron spectroscopy. Large quantities of high purity zinc oxide and magnesium oxide powders were synthesized for use as metal cluster supports. The MgO powders were well defined cubes with (100) surface exposure. Reaction conditions for the production of MgO were adjusted to minimize the terracing of the cubes and try to achieve a small cube size distribution. ZnO powders were far more varied than the MgO powders. ZnO produced using the method described here can assume a variety of morphologies, such as hexagonal pillars or plates, kites, tetrapods, needles, and less well defined shapes. Reaction conditions were adjusted so that batches with a high fraction of tetrapods and needles were synthesized. Batch composition was initially determined with electron microscopy, and this was correlated with the room temperature photoluminescence spectrum of the powders. The photoluminescence response consisted of a sharp peak at 380 nm, which corresponds to the band gap of the material, and a visible peak centered at 440 nm. This visible peak is located at a lower wavelength than many of the ZnO structures in the literature, which exhibit a peak in the green region of the visible
spectrum. The exact defects associated with the observed peak are not known, but may be caused by oxygen vacancies or zinc interstitials.

The metal oxides were decorated with palladium (ZnO and MgO) and gold (ZnO) clusters that were \( \sim 5\text{–}10 \text{ nm} \) in diameter. These materials were characterized with SEM, TEM (for Pd on MgO), and XPS. SEM imaging indicated that palladium clusters wet the ZnO substrate, which indicated a strong interaction between these two materials. Gold on ZnO did not exhibit such strong wetting. Palladium on MgO appeared to at least partially wet the support. XPS of these materials indicated that the palladium metal clusters were fully reduced. The electronic state of the gold was not unambiguously determined due to an overlap of the gold and zinc peaks. All of the XPS indicated that there might be carbon or hydroxyl compounds on the surface of the supports, which could have been introduced during the metal decoration process. Palladium/ MgO powders showed an especially large oxygen peak which indicates that, despite efforts to prevent the hydroxylation of the MgO during decoration, significant surface contamination may have occurred.

The behavior of hydrogen adsorbed onto these materials was studied using high resolution adsorption isotherms, and, for ZnO and Pd/ZnO, inelastic neutron scattering. The adsorption isotherms utilized normal hydrogen, while the inelastic studies used hydrogen that had been fully converted to the \( J = 0 \) ground para state.

The isotherms of hydrogen on ZnO showed multiple features, which is not likely attributable to phase or layering transitions. Those are usually observed on materials with single facet exposure, and these ZnO powders have multiple facets exposed. A possible explanation could be that the multiple exposed surfaces have different binding energies, and the features correspond to the preferential adsorption onto the highest binding energy site first, and then adsorption onto less preferable sites. The thermodynamics calculated from these isotherms indicate heats of adsorption that are consistent with physical adsorption (well below 20 kJ/mol).

Inelastic neutron scattering of para hydrogen films adsorbed on these ZnO powders were recorded for several hydrogen coverages. These results show a \( \text{para} \rightarrow \text{ortho} \)
transition peak centered at 14.7 meV that occupies a wide energy transfer range. The peak position corresponds to 3D free rotor hydrogen molecules, which shows that the interaction between the hydrogen and the ZnO did not significantly hinder the rotation of the hydrogen molecule. This corresponds to the weak interactions associated with the physisorption of molecules. The wide nature of the P→O peak may confirm what the adsorption isotherms suggested - that there are multiple adsorption sites on the ZnO powders which have different binding energies associated with them. The different binding energies can result in P→O transition energies that may be slightly greater or smaller than the energy at the peak center. This superposition of multiple energies results in a broadened transition peak. The combined adsorption isotherm and INS results indicate that, for the temperatures and pressures studied, hydrogen is physically and molecularly adsorbed, possibly onto multiple sites with different binding energies.

The weak physisorbed behavior of hydrogen on bare ZnO contrasts with the behavior of hydrogen on palladium decorated ZnO. The information that can be extracted from the isotherms is somewhat limited by the heterogeneity of the surface, but the isosteric heats of adsorption for normal hydrogen do correspond with physical, not chemical, adsorption. The inelastic neutron scattering response of a single coverage of para-hydrogen was measured, and offers additional information about the adsorbed film behavior. The P→O transition peak is sharp and narrow, and is located at 6.5 meV. A strong hydrogen-surface interaction can hinder the rotation of a hydrogen molecule to such an extent that it behaves as a two-dimensional rotor, in which case the P→O transition energy would be expected to equal the rotational constant, \( B \). The expected value of \( B \) for hydrogen is 7.35 meV, so the additional shift to an even lower energy indicates that not only is the hydrogen molecule behaving as a 2D rotor, but the H-H bond length has also extended by 6.2 % to 78.7 pm. These results indicate that the hydrogen-surface interaction is strong enough to significantly hinder the hydrogen rotation, and the additional extension of the molecular bond length also indicates that there may be some electron transfer from the hydrogen
molecule to the surface. This type of donation from a hydrogen molecule to a metal has been previously documented in the Kubas compounds that were briefly discussed. The P→O peak has a sharp shape corresponding to adsorption on a single site (as compared with the peak shape for H$_2$ on bare ZnO), and this single site is most likely the palladium metal clusters. The behavior suggested here was observed in computer simulations of hydrogen molecules on Pd/ZnO (performed by E. Cruz-Siliva, see section 4.2.2), which showed adsorbed hydrogen with an extended bond length on the metal site.

The behavior of hydrogen on gold decorated ZnO and palladium decorated MgO have not been as thoroughly characterized as the ZnO and Pd/ZnO systems, but adsorption isotherms have provided some insight into these systems. The isosteric heats of adsorption of normal hydrogen on Au/ZnO correspond to physical adsorption, and exhibit an increase near monolayer completion, and then a smooth decrease and approach towards the bulk heat of hydrogen. The isosteric heats for normal hydrogen on Pd/MgO can be compared to the isosteric heats of Pd/ZnO, and it does not appear that the Pd/MgO system displays the additional rise and fall in the isosteric heat that Pd/ZnO shows after monolayer completion. This is an indication that hydrogen adsorption on different palladium decorated supports exhibit different behavior. The hydrogen on Pd/MgO system also shows a change in the shape of the isotherm near the saturated vapor pressure as temperature is increased. The exact nature of this behavior change cannot be determined from isotherms alone, but perhaps as temperature and pressure increases there is some chemical modification taking place in addition to physical adsorption.

The work discussed here reflects initial investigations of the metal decoration of metal oxides. There are many avenues that can be followed to continue to develop an understanding of the behavior of metal clusters on metal oxide supports. Studies could initially be expanded to investigate additional gas coverages of para-hydrogen on Pd/ZnO - as coverage increases, would other adsorption sites be observed in the inelastic response of the film? Also, neutron scattering investigations of
hydrogen adsorbed onto Pd/MgO and Au/ZnO would provide information about
the microscale hydrogen-surface interactions of the materials that would compliment
the thermodynamic information.

In addition to an extension of the inelastic studies of para-hydrogen on these
materials, the neutron scattering response of normal hydrogen could be measured.
The neutron studies presented here all used para-hydrogen, where the hydrogen
molecules were in their lowest rotational ground state. Normal hydrogen consists
of a mix of both para and ortho molecules, so some of the adsorbed gas would not be
in the rotational ground state. How would the additional energy of molecules not in
the $J = 0$ state affect the observed hydrogen behavior?

This work could also be expanded to the deposition of metals onto other metal
oxide supports, which would provide additional comparative information about the
interactions between clusters and their supports. In additon, an issue that was raised
in this work was whether the solvents used to deposit the clusters damages the
supports. This could be avoided if metals were deposited using a solvent-free method,
such as sputtering the metals onto the supports using a magnetron sputtering gun.
This method presents challenges as well, such as how to deposit the clusters onto the
powders in a uniform fashion, and how to control the cluster size.

These investigations can also be extended to include applications of the metal
decorated metal oxides. Gold decorated ZnO has already been tested and shown
to be active in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol
[Chen, H. et al., manuscript in preparation]. The activity of the catalytically active
metals used here could also be tested in additional reactions, such as the water-gas
shift, partial oxidation of methanol, and steam reformation of methanol, which are
all relevant for the production of hydrogen. The future work discussed here would
help inform a description of the interaction between metal clusters and metal oxide
supports, and how this interaction can affect the gas adsorption and catalytic activity
of these materials.
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Vita

Paige Landry was born May 25, 1983 to Dennis and Joann Landry in Massachusetts. Her family moved frequently and lived in several locations along the eastern coast. She attended Fairfax High School in Fairfax, Virginia and Coventry High School in Coventry, Rhode Island. She graduated from Fairfax High School in 2001. She then attended Virginia Tech, where she pursued a Bachelors of Science in Chemistry, a Bachelors of Arts in Physics, and a Mathematics minor. She completed her studies there in 2005. During her time at Virginia Tech, she worked in the research laboratories of John Morris (Chemistry) and William Spillman (Physics). After completing her undergraduate work, she joined the University of Tennessee Chemistry graduate program in 2005 to join the Larese group and pursue her Doctoral degree.