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Fundamental Insights into Catalyst Design: Energetics of Metal Atom Adsorption
and Nanoparticle Adhesion on Oxide Surfaces

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Abstract

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Heterogeneous catalysts consisting of transition metal nanoparticles dispersed on high-surface-area oxide supports are ubiquitous in industrial-scale chemistry and alternative energy technology. Despite their importance, our fundamental understanding of the physical and chemical properties that render these systems catalytically effective is still incomplete. This dissertation details the use of surface-sensitive ultrahigh vacuum (UHV) techniques to study model catalysts consisting of late transition metals that are vapor-deposited onto single-crystal oxide films in order to understand how their fundamental physical and chemical properties affect their catalytic properties, such as activity, selectivity, and resistance to deactivation.

Specifically, the binding energies of metal atoms and nanoparticles – and the adhesion energy of metal nanoparticles and films – are measured as a function of the size and type of nanoparticle, and the surface or site that they are adsorbed on. The key technique utilized in this study is single-crystal adsorption calorimetry (SCAC), which uses a highly sensitive detector to

directly measure the heats of adsorption of metal vapor adsorbing onto oxide thin films. Calorimetric data are combined with surface-sensitive spectroscopic techniques to characterize the oxide surface, and to model the size of the nanoparticles as a function of total metal coverage. This approach allows the calorimetric data to be correlated with the surface structure, composition, particle size, or electronic character of the system. Several improvements to the instrument are discussed that allow for the study of metals with very low vapor pressures (high heats of vaporization), specifically Au, which is the focus of this work. This new instrument can be operated at temperatures as low as 100 K. This temperature is used to study metal atom adsorption under conditions where adatom diffusion is slower, which increases the particle density (reducing the size of particles formed) and increasing the likelihood that nucleation occurs at less favorable sites.

This dissertation discusses Au adsorption on three different surfaces with increasing complexity: Pt(111), MgO(100), and CeO_{2-x}(111). Results are compared to Cu adsorption on Pt(111) and CeO_{2-x}(111) (also presented in this work), and to Cu adsorption on MgO(100) as well as Ag adsorption on MgO(100) and CeO_{2-x}(111) (from previous work by this research group). The first experimental measurements of gold adsorption onto an oxide surface as a function of particle size are presented, and the adsorption energies of both a single Au atom and a single Cu atom were measured on CeO_{1.95}(111). This research represents the first experimental measurements of any metal atom adsorption onto any oxide surface. The effect of defects on Au and Cu adsorption, such as step edges and electron-rich oxygen vacancies is discussed in detail. These defects are either introduced in film preparation (in the case of oxygen vacancies on CeO_{2-x}(111)), or are inherently present in thin film preparations (morphological defects). The metals studied here, like most late transition metals, adsorb more strongly on morphological defects such as steps, while only Au and

Ag bind more strongly to oxygen vacancies on $\text{CeO}_{2-x}(111)$ (whereas Cu does not). Additionally, Au was found to nucleate significantly more strongly than Ag and Cu on morphological defects of $\text{MgO}(100)$, and to form 2D islands on $\text{MgO}(100)$ within the first 0.4 monolayers (ML) coverage. This work presents the first measurement of the heat of adsorption (and thus the chemical potential) of metal atoms in metal nanoparticles as a function of their 2D island diameter. A similar method of analysis is used to discover the chemical potential of Cu atoms in Cu nanoparticles as a function of their 3D particle diameter on $\text{CeO}_{2-x}(111)$. The work contained in this dissertation has added critically important thermodynamic and structural data to the library of research in the catalysis and surface science communities, and has addressed some of the most relevant materials that could not be studied with previous generations of SCAC instruments. The model catalyst systems in this dissertation are of substantial fundamental and practical interest due to their immediate use in industrial catalysis. By combining these newest results with existing data (both from this research group and from the literature) we have proposed a new trend for metal-oxide adhesion. These investigations, and specifically this new proposed trend, will aid in the global effort to expedite the design and testing process of new catalytic materials through improved understanding of their fundamental properties.

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CHAPTER CONTRIBUTIONS

The work described in Chapter 2 represents the collaborative efforts of Dr. Jason Farmer, Dr. Jason Sellers, Dr. Trevor James, and myself to design and improve the newest generation Calorimeter. All of the authors listed contributed to building, installing and testing work conducted on this instrument from 2008-2012. The relative work contributed follows the order of authorship listed in Chapter 2. Each author also conducted a variety of experiment, and contributed intellectually to writing of this Chapter as presented in this dissertation. Several sections of this writing are my original work, and other sections have been reproduced with permission from the authors of the paper listed, and the American Institute of Physics (from Review of Scientific Instruments).

Chapters 3 and 4 are my primary work, with assistance in data collection and workup by Dr. James and Gabriel Feeley. The data contained in these chapters represents three-to-ten total repetitions of each experiment, with data collection often spanning multiple days. Many of these experiments require the presence of two people. On several occasions, this second person was an undergraduate research assistant, Ashley Tilson (Chapter 3) or Naomi Miyaki (Chapter 4). Each experiment was conducted at least once by each author listed, and I supervised ~90% of experiments conducted. Data analysis was independently conducted by both me and by the second author (Dr. James in Chapter 3, Gabriel Feeley in Chapter 4) so that they could be compared for accuracy. I contributed the primary intellectual work and writing for these two chapters, with consultation, discussion, and regular feedback provided by the other authors.

In Chapter 5, Dr. James was the supervising lead on these experiments, and I assisted with data collection, data workup, and intellectual discussion that lead to the two papers contained within this section. The published writing in this Chapter has been reproduced with permissions from the authors and ACS publications.

Chapter 6 is the result of intellectual discussions between myself and Dr. Charles Campbell, and contains references to work done by Dr. James. The work in Chapter 7 is divided similarly to Chapter 5, where Dr. James is the primary author and contributor to the work on Cu / Pt(111) while Gabriel Feeley is the first author of the work on Au / Pt(111), which was used as a training project under my supervision. My contributions were made in data collection, intellectual discussion, and experimental guidance. This work was supervised by Dr. Charles Campbell.

Chapter 8 describes work that was conducted at the Fritz Haber Institute in Berlin Germany, and is the primary intellectual work of Dr. Petr Dementyev, who supervised my training and operation of the instrument used for this work. I was responsible for growing and preparing thin $\text{Fe}_3\text{O}_4(100)$ films reflectivity measurements as described in Chapter 8.. Calorimetry measurements were conducted primarily by Dr. Dementyev. The primary author of this work is Dr. Dementyev, and some of this text has been reproduced with his permission and the permission of Dr. Hans-Joachim Freund, the director of the Chemical Physics department of the FHI. The supervising PI of this work was Dr. Swetlana Schauer mann. Other sections of this text describing the preparation of these $\text{Fe}_3\text{O}_4(100)$ films (and some of the figures in Chapter 8) has been reproduced with the permission of Earl Davis and Elsevier.

Chapter 1. Introduction

In 1798, economist Thomas Robert Malthus observed that the world's population grows geometrically, while food supplies grow only arithmetically, therefore human population is controlled by cycles of famine and disease. While the “Malthusian catastrophe” predicted that a growing demand for food would soon exceed humans' capacity to produce,¹ this doom was circumvented in the early 20th century by German chemist Fritz Haber, who developed a process to synthesize a bioavailable, easily-deliverable source of nitrogen fertilizer (ammonia) from atmospheric nitrogen and hydrogen using one of the world's most famous heterogeneous catalysts.

Heterogeneous catalysts play an enormous role in the modern world. In 2013 in the United States, chemical production made up approximately 10% of the US Gross National Product, and was responsible for roughly a quarter of the country's total manufacturing energy consumption.² Ninety percent of all chemical industrial processes in the United States use catalysts, and eighty percent of these are heterogeneous.² One of the most common families of heterogeneous catalyst materials consists of transition metal nanoparticles dispersed across high-surface-area oxide or carbon supports. These materials can be found in a number of current and emerging energy technologies; they improve fuel efficiency, aide industrial-scale chemical production, convert environmental pollutants to benign chemicals, and bolster clean emission technology. These same materials are also used in fuel cells as electrocatalysts, in solar cells as photocatalysts, and in green chemistry.³⁻⁷ Because the environment of a heterogeneously catalyzed reaction is highly complex – occurring at the interface of two or sometimes three different phases of matter – many catalysts of this type in use today are not well-understood at a fundamental level. Therefore, it can be difficult to deduce why some materials are superior to others for specific applications, or why some

have longer lifetimes. Despite a large degree of recent attention in the past several decades, there still is a great global need for fundamental research in the field of heterogeneous catalysis. By understanding how and why a catalyst works, the scientific community can help guide the rational design of improved catalytic materials for a broad range of applications. The work presented in this dissertation is part of a broad effort to use surface-sensitive techniques and well-controlled model systems to build a rigorous fundamental understanding how interactions at the metal/support interface (such as binding, charge transfer and adhesion energy), as well as other physical/chemical properties, relate to the activity, selectivity, and lifetime of catalytically relevant supported metal oxide catalysts. Specifically, this work focuses on the thermodynamic and structural properties of supported gold nanoparticle model systems using a novel Ultrahigh Vacuum (UHV) technique called Single Crystal Adsorption Calorimetry (SCAC) coupled with a detailed analysis of surface structure using spectroscopy.

The research in this dissertation is of particular importance because supported gold nanoparticles have attracted significant attention in the last decade as potential low-temperature catalysts for selective oxidations and other industrially relevant reactions. They are also used in the fields of photonics, plasmonics, nanotechnology, and biology. The effectiveness of supported metal nanoparticles comes in part from the high surface-to-volume ratio of nanoparticles, which maximizes the number of reactive surface sites per quantity of material used. However, recent progress in nanotechnology has revealed that the catalytic performance of these nanoparticles (both activity and selectivity) can vary dramatically with particle size between 1 and 10 nm.^{8–11} Indeed, while gold is inert in its bulk form, it becomes catalytically active at the nanoscale for a variety of different reactions.^{12–16}

Gold has long been prized for its beauty and worth, which is due in part to its durability. Unlike all other transition metals, it does not oxidize in atmosphere. Relativistic effects must be considered in the description of its electronic structure due to the large charge of its nucleus. The *s* and *p* orbitals contract in response to the large nuclear charge, while the *d* and *f* orbitals expand. Indeed, when gold is modelled without relativistic effects, the calculated energy difference between the 6*s* and 5*d* orbitals is larger by nearly 60%.¹⁷ As result of these relativistic effects, the gold 5*d* band is heavily involved in its chemistry. For example, the increased participation of the *d* orbitals in metal-metal bonding helps explain the high bulk cohesive energy of gold (368 kJ/mol¹⁸) compared to silver (285 kJ/mol¹⁸).¹⁹ Gold also has the highest electronegativity of any metal, an extremely high electron affinity (2.31 eV), and a similarly high ionization potential (9.22 eV).²⁰ Gold is the only transition metal that does not have a stable oxide,²¹ and it has a unique ability to interact with itself in a property which is called aurophilicity.²²

While gold atoms can display rich organometallic and coordination chemistry,²³ solid gold surfaces are typically not reactive. However, due in large part to the seminal work of Masatake Haruta, the last three decades of scientific research have revealed that gold particles that are smaller than 10 nm in diameter can demonstrate chemical and physical properties that are unique from the bulk. In 1989, Haruta et al.²⁴ showed that gold nanoclusters prepared on several different metal oxide supports were catalytically active for both CO oxidation and propylene epoxidation. Most notably, these reactions occurred at low temperature – as low as 200 K for CO oxidation,²⁴ compared to nearly 500 K required for the Pt-, Pd-, and Rh-containing materials used in current catalytic converters. Since then, gold nanoparticles have attracted a significant amount of attention.

Despite this attention, the nature of small supported gold nanoparticles – and indeed other supported transition metal nanoparticle materials – is still unclear. There have been enormous

efforts to draw correlations between catalytic properties and the electronic and structural properties of Au surfaces and particles, as well as to the size of the Au particle, and to the material that it is supported on (reviews of both experimental and computational efforts to determine these correlations can be found in References ^{12,14,19,25–28}). Yet even with these efforts, the picture is often still obscured, especially given that these properties are often not entirely independent from each other. For instance, the support material can affect the electronic structure, size, and shape of the metal nanoparticle, and it may also contribute directly to the catalytic reaction, or generate new sites at the interface. Supported gold nanoparticle systems have also proven to be exceptionally challenging to model with Density Functional Theory (DFT) due to gold's unique chemistry described above, and the results are often highly sensitive to the choice in DFT functional.^{29–32}

Because gold displays the most dramatic size-dependent properties of any of the late transition metals,²⁵ stabilizing gold nanoparticles at their optimum size for peak performance is critical if they are to be used in practical industrial applications. However, for late transition metals, the bulk phase is more thermodynamically stable than highly dispersed nanoparticles; the metal-metal bond is stronger than the metal-oxide bond, and the excess of under-coordinated surface atoms drives small particles to agglomerate and form larger particles over time.^{33–36} This coarsening process is the primary cause of catalyst deactivation.^{37,38} Certain support materials, such as cerium oxide (ceria) are known to promote greater resistance to nanoparticle coarsening than others.^{39–41} (It should be noted that the terminology used here, i.e. coarsening, agglomeration, and sintering, encompasses many different mechanisms by which deactivation can take place, such as by Ostwald ripening, or by diffusion of particles and coalescence.^{34,36,42}) However, the kinetics of these deactivation processes and their dependence on the physical parameters of the support such as structure and composition are not well understood. This makes the testing of new catalytic

materials difficult and time-intensive. Ideally, a kinetic model could predict catalyst lifetime based on initial measurements, which would not only predict longevity, but could also expedite the design and testing of new catalytic materials with improved resistance to deactivation.

The choice of support can dramatically affect the catalytic properties of the supported metal nanoparticle,^{13,27,43–48} but the details of the nanoparticle-support interaction are still unclear.⁴⁹ The support may alter the electronic character of the particle,¹⁹ change its shape or size, participate directly in the reaction,⁵⁰ provide supplementary binding sites,⁵¹ or generate unique electronic structure at the interface.⁵² Metal oxides are often used as supports, however their surfaces are often far more complex than metal surfaces, and in real applications they are often highly faceted, making it challenging to clarify structure-function relationships. Therefore, given the high degree of complexity of real catalytic materials in their native environment, scientists often construct model systems to isolate individual phenomena in order to better understand the properties of these types of oxide-supported metal nanoparticle materials.

This work utilizes one of the simplest types of model system that can be constructed to study heterogeneous catalysts. In these models, metal atoms are deposited in controlled quantities onto structurally well-defined single-crystalline surfaces in ultrahigh vacuum (UHV).^{53–55} This experimental system provides a clean, controlled environment that eliminates contributions from the air or liquid interface. As a result, correlations are revealed between the chemical and physical properties of the catalyst – such as particle morphology, redox behavior, acid/base characteristics, defect concentration, electronic structure, the size/type of metal nanoparticle, and the size and type of atom to which nanoparticles bind – and the catalytic properties of the system.

Using this model approach, measurements of the energetics of the interfacial interactions between the nanoparticle and its support are collected, and then coupled with detailed structural

characterization using spectroscopy. Since the difference between the internal energy of a metal particle on a surface and the energy of its bulk drives coarsening, the coarsening rate and optimum particle size will depend on the strength of the interaction between the nanoparticle and the surface. Previous research conducted in the Campbell group shows that particle binding energies appear as “activation energy” terms in the kinetic rate equations.^{33,35} Additionally, knowing the strength of binding between the nanoparticle and the support can provide information about the chemical potential of the particle,⁵⁶ which in turn provides insight into its ability to bind small molecules and catalytic intermediates.^{35,39,52,56,57} The adhesion strength of the nanoparticle to its support can also affect the particle size and shape,^{42,58,59} which affects the number and type of undercoordinated atoms in the particle, which in turn can affect catalytic properties.

Adsorption energies have traditionally been measured using indirect methods such as temperature programmed desorption (TPD) and equilibrium adsorption isotherm analysis (EAI). The group of the late D. W. Goodman has contributed a significant number of groundbreaking and elegant TPD experiments to this field, including measurements on Au supported on TiO₂(001) / Mo(100)⁶⁰ and on disordered SiO₂ / Mo(110).⁶¹ These techniques, while usually quite valid, suffer when the adsorption-desorption process is not reversible. During the heating of TPD prior to desorption, transition metal nanoparticles and submonolayer metal films on oxide surfaces often irreversibly sinter or agglomerate into large particles that cover much less than 100% of the oxide at temperatures below that at which desorption occurs. Therefore, the coverage-dependent heats of adsorption and adhesion extracted from TPD provide only upper limits.⁵⁶ Therefore, a method of direct energy measurement is required in order to obtain particle size-dependent energetics to understand the properties of this family of heterogeneous catalysts.

To accomplish this, the Campbell group pioneered the development of a novel UHV technique called single-crystal adsorption calorimetry (SCAC) based on the ground-breaking method of Sir David King.^{62,63} This technique – which will be discussed in detail in Chapter 2 – utilizes a highly sensitive, flexible heat detector to measure minute temperature changes upon the adsorption of metal atoms or molecules deposited on single-crystal oxide substrates. With this experimental system, it is possible to directly measure adsorption energy on well-defined surfaces. These measurements are combined with spectroscopically measured structural information about the system, which together clarify the structural dependence of these energetics.

The work presented in this dissertation adds critical data to a large-scale effort by the Campbell research group to use model catalysts to investigate how interfacial interactions such as binding and adhesion energy, as well as other physical/chemical properties, relate to sinter resistance, activity, and selectivity of catalytically relevant metal nanoparticle / oxide support systems. This is achieved by studying the effects of three variable parameters: the type of metal atom, the type of support material, and the chemical state of the support material surface. Prior to this work, the Campbell group published SCAC results for Cu, Ag, Pb, Ca and Li adsorption on MgO(100)^{64–68} to investigate the effect of varying the metal atom on the same surface. Through these prior SCAC studies and the collection of other UHV results, Sellers and Campbell proposed a linear trend between the adhesion energy of late transition metals to MgO(100) and the energy of formation of the metal's most stable oxide from gaseous atoms, which will be discussed in further detail in Chapter 8.⁵⁶ The adsorption of Ag on Si(111),⁶⁹ CeO₂(111),⁷⁰ and Fe₃O₄(111)⁷¹ was also studied by the Campbell group to examine the effect of the support, which resulted in a relative ranking of the adhesion capability of different metal-oxide support surfaces.⁵⁶

However, these efforts were limited by the capabilities of the metal atom source (a Knudson cell) in the original metal atom SCAC instrument.⁷² This source could not reach temperatures high enough to evaporate more catalytically active metals with low vapor pressures and the most interesting chemistries, such as Pt, Pd, and in particular Au, without overwhelming the signal with background radiation. To address this, the group's newest calorimeter implemented a directed electron-beam heated metal atom source along with several other improvements for growing and studying oxide surfaces.⁷³ The results in this dissertation on supported gold nanoparticle systems presented are therefore built on more than a decade of instrumental development and scientific advancement in SCAC-measured energies in the Campbell group.

The focus of this dissertation is the adsorption and adhesion of Au atoms and nanoparticles to three different surfaces with increasing complexity: Pt(111) (a single-atom metal), MgO(100) (a binary, non-reducible oxide) and CeO_{2-x}(111) (a binary reducible oxide). Results from these system are compared to work presented here for Cu on CeO_{2-x}(111), as well as to the group's previous results for Ag on CeO_{2-x}(111),⁷⁰ Cu on MgO(100),⁷⁴ and Ag on MgO(100).⁶⁷ The new instrument can also conduct calorimetric measurements at cryogenic temperatures where metal diffusion is greatly reduced, which allows for the measurement of adsorption energies on smaller clusters that more accurately represent metal-oxide binding with minimal metal-metal interaction. Using this capability, this dissertation reports the first ever measurement of the binding energy of any isolated late transition metal adatom to any oxide surface for Cu on CeO_{1.95}(111) (Chapter 5), and for Au on CeO_{1.95}(111) (Chapter 3). These results provide a direct comparison to DFT energies for benchmarking applications.

In Chapter 3, the adsorption of Au on reduced CeO_{2-x}(111) surfaces is investigated. It is determined that like Ag, Au binds more strongly to more reduced surfaces, indicating stronger

binding to oxygen vacancies. In Chapter 4, the adsorption of Au on MgO(100) reveals that Au forms 2D islands at low coverages due to strong binding at morphological defects, which represents the first measurement of the adsorption energy of a 2D island as a function of its diameter. These data also present the first opportunity to directly compare adhesion energies measured by calorimetry with those measured by a contact-angle technique (Transmission Electron Microscopy^{75,76}). The difference between our calorimetrically determined adhesion energies and the value found by TEM indicates that our 300 K measurements are due to Au particles that nucleated at defects, while at 100 K they are from Au particles nucleated at terraces. Chapter 5 presents the adsorption of Cu on reduced CeO_{2-x}(111), which reveals that Cu binds *less* strongly on more reduced surfaces, *unlike* Au and Ag. Chapter 6 presents a comprehensive comparison of the three metals in group 13 of the periodic table (Cu and Au, and Ag) on these two oxide surfaces. This comparison is used to propose a trend line for the adhesion of these metals to CeO_{2-x}(111) using the same relationship as the trend line proposed for MgO(100) described above.⁵⁶ Because these two lines have the same slope, this relationship can be extended to other metal-on-oxide systems where only a single data point is known. This relationship represents the culmination of over 15 years of calorimetric results from this group and the efforts of surface science groups around the globe, and it is a significant step forward in construction of a systematic trend with predictive power for the rational design of improved materials.

In Chapter 7, the adsorption of Au on Pt(111) is discussed as a model bimetallic system, which provides valuable information about catalytically relevant bimetallic nanoparticles. This work is compared to the adsorption of Cu on Pt(111). Despite the fact that these two atoms (Au and Cu) lie in the same column of the periodic table, they exhibit different behavior due to a difference in size and lattice strain induced by the Pt(111) substrate. Finally, Chapter 8 presents

research that was conducted at the Fritz Haber Institute in Berlin, Germany, under the guidance of Dr. Svetlana Schauermann, Prof. Dr. Hans-Joachim Freund, and in collaboration with Petr Dementyev. This work was conducted during a four-month collaboration using a calorimeter that is similar to the one used in the Campbell group. This instrument, which is described in detail, was used to study the adsorption of water onto magnetite $\text{Fe}_3\text{O}_4(100)$ in order to investigate the dissociative adsorption of water as hydrogen and hydroxyls. This surface is the second single-crystal magnetite surface that has been studied using this technique for water adsorption, and the results are compared to $\text{Fe}_3\text{O}_4(111)$. This work constitutes the first direct comparison of the same adsorption process on two different surfaces of the same oxide material. Real catalyst materials are powdered and expose multiple different surface facets; therefore, knowing which surfaces are the most active for water splitting can help improve our understanding of how this reaction takes place, what the catalytically active sites are, and how to optimize the availability of the most active surface when designing real catalysts.

By combining energetic measurements with advanced surface analysis techniques, the binding strength of small particles is directly measured versus their size. From these results, it is possible to determine how the heat of adsorption depends on the size and type of nanoparticle (down to the single-atom limit), the site to which it binds, and the physical or chemical properties of the support. The results of this dissertation have been analyzed to find quantitative trends across different metal/oxide systems to help build a predictive model for sintering, and assist in the global effort to develop new materials with increased activity, selectivity, and lifetime.

Chapter 2. Apparatus and Experimental Details

Portions of this chapter have been published as:

Sellers J.R.V.; James, T.E.; Hemmingson, S.L.; Farmer, J.A.; Campbell, C.T.

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Thin films of metals and other materials are often grown by physical vapor deposition. To understand such processes, it is desirable to measure the adsorption energy of the deposited species as the film grows, especially when grown on single crystal substrates where the structure of the adsorbed species, evolving interface, and thin film are more homogeneous and well-defined in structure. The Campbell research group previously developed an adsorption calorimeter capable of such measurements on single-crystal surfaces under the clean conditions of ultrahigh vacuum (UHV).⁷² The operation of an improved calorimeter is described in brief here, with a description of the improvements that allow for heat measurements with ≈ 18 -fold smaller standard deviation and measurements of the adsorption of lower-vapor-pressure materials which would have previously been impossible. These improvements are accomplished by: (1) using an electron beam evaporator instead of a Knudsen cell to generate the metal vapor at the source of the pulsed atomic beam, (2) changing the atomic beam design to decrease the relative amount of optical radiation that accompanies evaporation, and (3) adding an off-axis quartz crystal microbalance (QCM) for real-time measurement of the flux of the atomic beam during calorimetry experiments.

2.1 INTRODUCTION

Thin films of metals and other materials are grown by physical vapor deposition for a wide variety of technological applications, for example in the fabrication of microelectronics and computer parts, solar cells, light-emitting diodes, reflective and protective coatings, chemical

sensors, and electrodes of various types. Thin films and nanoparticles are also grown by physical vapor deposition for a wide variety of fundamental research applications aimed at studying the properties of surfaces, interfaces, nanoparticles, and nanomaterials. A great deal of basic understanding of the film growth process, the thermodynamic stability of the resulting films or nanoparticles, and the strength of chemical bonding at the resulting interface(s) is provided by measuring the adsorption energy versus coverage during such deposition processes.^{35,39,72,77,78}

The strengths of chemical bonding at interfaces between materials have a remarkable impact on almost all areas of science, technology, and industrial manufacturing.⁷⁹ The adhesion energy between two solids can also be determined by measuring the adsorption energy versus coverage during vapor deposition,⁷⁷ even in cases where the deposited material grows as nanoparticles rather than a continuous film.⁶⁷ Adhesion energies define the relative stability of the interface, control the mechanical properties of composite materials, and define the shape of supported nanoparticles such as, for example, those used in catalytic or fuel-cell materials consisting of metal nanoparticles supported on high-area oxide or carbon supports.⁴² In this latter example alone, the adhesion energy also dictates how the chemical potential of the metal atoms depends on the particle size and support material, which in turn controls catalytic reactivity and its deactivation by coarsening or sintering.⁵⁶

Thus, there is great motivation to measure adsorption energies during physical vapor deposition of one material onto another. Such measurements are particularly enlightening when performed on the clean surface of a single crystal of the substrate material, since this enables better structural homogeneity and structural characterization of the adsorbed precursors, nanoparticles, and thin films whose energies are being measured.^{53,80,81}

To address these important concepts, our group designed and built the first adsorption calorimeter capable of such measurements of metal adsorption energies on single-crystal surfaces in a ultrahigh vacuum (UHV) chamber where the substrate surface cleanliness and the structure of the resulting thin film or nanoparticles could also be measured with surface analysis techniques.⁷² This chapter describes a new apparatus that incorporates several major improvements to the capabilities of that original design. These improvements decrease the pulse-to-pulse standard deviation of the metal adsorption energy measurements by ≈ 18 -fold, while also allowing for measurements of the adsorption energies of metals which would have been impossible to study with our earlier design, namely metals with very low vapor pressures or high heats of sublimation (e.g., Pt, Au, Pd, Rh, etc.).

The ability to determine heats of adsorption on clean surfaces of single crystals in UHV is not new. Techniques such as temperature programmed desorption (TPD) and equilibrium adsorption isotherm (EAI) analysis have often been used to measure adsorption properties of atoms and molecules on single-crystalline supports. However, with these techniques, heats of adsorption are measured indirectly in a way that requires completely reversible adsorption. In cases where adsorption is not reversible, a technique for directly measuring heats of adsorption is necessary. Single crystal adsorption calorimetry (SCAC) was developed for such cases.⁶² This approach is particularly important for studying metal adsorption and metal thin-film growth, since metal adatoms frequently sinter into very large particles or diffuse into the substrate upon heating at temperatures well below those necessary for desorption.^{35,82} This was the motivation for designing the original SCAC instrument mentioned above for metal vapors.^{72,77} Subsequently, it has been employed to measure the adsorption energies of several metals on a variety of different single

crystal surfaces as a thin metal film is grown and the metal / substrate interface is formed.^{39,64-67,74,83-86}

This chapter describes the newest calorimeter for SCAC of metal adsorption energies which offers several important advantages over the previous design. It uses an electron beam evaporator as the metal atom source instead of the Knudsen cell previously used. This localizes the heat input to the surface of the metal melt and produces much less optical radiation than the Knudsen cell type metal vapor source, thereby increasing the signal/noise of the calorimetry measurements. The atomic beam design was also modified to further decrease the relative amount of optical radiation that accompanies evaporation. In addition, an off-axis quartz crystal microbalance (QCM) was added for real-time measurement of the flux of the atomic beam during calorimetry experiments. These improvements allow more sensitive and accurate measurements of metal adsorption energies and the interfacial bonding strengths of a wider variety of metal / support systems.

2.2 THE UHV CHAMBER

The instrument operates in a UHV chamber with a typical base pressure below $\approx 1 \times 10^{-10}$ Torr that is equipped with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), low-energy ion scattering spectroscopy (LEIS), a quadrupole mass spectrometer (QMS), and two quartz crystal microbalances (QCM). Surface spectroscopy signals are obtained by a PHI 10-360 precision energy analyzer equipped with a PHI 72-250 position-sensitive detector. The instrument also includes a sample preparation chamber that can be closed off with a gate valve during preparation of the single crystal's surface in order to protect the UHV conditions in the calorimeter and surface analysis region. Single crystals can be translated to different regions of the instrument with a fourfold-axis manipulator.

During metal deposition and calorimetry experiments (see below), the sample and the heat detector are both held in contact with the same thermal reservoir that can be cooled by liquid nitrogen. The temperature is monitored by two type-K thermocouples attached to the sample holder and to the PVDF ribbon holder near the sample. At all other times, the sample is mounted onto a translatable and rotatable manipulator fork that can be similarly cooled to 100 K by a liquid nitrogen reservoir. The temperature of the manipulator fork is also monitored by a type-K thermocouple spot-welded near the sample.

2.3 SURFACE CHARACTERIZATION

The growth morphology of metal nanoparticles on $\text{CeO}_{2-x}(111)$ was determined using LEIS and XPS with a 135 degree scattering angle. LEIS measurements are carried out using He^+ ions with 1.0 or 1.5 keV primary energy from a focused ion beam that is rastered rapidly over an area of 2 mm x 2 mm. Using a background of 2×10^{-7} Torr He and 3 mA emission current gives an ion current density of $\approx 90 \text{ nA/cm}^2$ averaged over the rastered area. XPS measurements are performed with an Al $K\alpha$ source that operates at 12 kV and 200 W. This combination of techniques provides detailed information on the surface structure, with XPS or AES analysis providing information on the elemental composition of a surface down to $\approx 3 \text{ nm}$ from the surface, and LEIS providing the elemental composition of the top-most atomic layer. The chamber is also equipped with a low-energy electron diffraction (LEED) screen, which allows for verification of the crystallinity of the sample and any thin film grown on its surface.

2.4 CALORIMETER

A general schematic of the calorimetry design can be seen in Figure 2.1. It consists of a pulsed metal atom beam and a thin pyroelectric polymer (polyvinylidene fluoride, PVDF) ribbon

heat detector that is pressed into the back of a 1 μm thick single-crystal Pt(111) sample, which is ≈ 8 mm in diameter. A 4-mm diameter, collimated and chopped metal atom beam is generated using an electron-beam evaporator. This results in a spatially and temporally well-defined 100 ms pulse that contains ≈ 0.02 ML of metal vapor dosed every two seconds onto the front face of the sample. A transient temperature change in the ribbon results in a measurable change in its face-to-face voltage whose magnitude is proportional to the heat released upon metal adsorption. The intimate thermal contact between the sample and the ribbon allows for the heat released from adsorption of a 100 ms pulse of gas to be detected almost instantaneously (i.e., with an instrument response time capable of detecting kinetic delays in heat deposition as short as 10 ms⁸⁷). With this setup, the heats of adsorption can be determined to within 3% accuracy in most cases and with a point-to-point standard deviation of only 0.6 kJ/mol when depositing 2% of a monolayer per pulse, and a temperature range of 100 to 350 K.⁸⁸

2.5 CALIBRATIONS AND CORRECTIONS

2.5.1 Laser Power Calibration

The detector response is calibrated before and after experiment using pulses of known energy from a HeNe laser (632.8 nm). The laser is directed through the molecular beam path using translatable mirrors where it is chopped and collimated in the same way as the molecular beam. The laser power is measured by translating a mirror just in front of the sample that reflects the laser beam through a chamber window where its intensity can be measured with a photodiode. This measured laser power is scaled by a known calibration factor (measured previously) to determine the power at the sample position. The final mirror is then retracted, and the laser pulses impinge upon the sample. The height of these resulting laser pulse signal in volts

can then be directly related to the laser power, and this contact value (V/J) remains constant as long as the detector remains in contact with the sample.

Not all of this laser power is absorbed by the sample, and this fraction is determined by the sample's reflectivity. For metals, this value is well known. However, it is difficult to directly measure both the initial optical reflectivity of the oxide-coated sample, which changes slightly from run to run due to differences in oxide film thickness, as well as the final reflectivity after metal deposition, which similarly varies slightly with final metal film thickness due to the high degree of surface roughness. Therefore, the absolute calibration factor in each run is typically estimated using the initial reflectivity at a single oxide thickness, and then performing the same laser calibration measurements on the sample both before and after metal deposition, assuming that the change in the sample reflectivity was the only parameter that changes the magnitude of the detector response to the laser. The calibration factor thus obtained was then corrected slightly so that the multilayer heat of adsorption in the high-coverage limit would equal to the literature value for the heat of sublimation of the bulk solid metal at the sample temperature.¹⁸

2.5.2 Optical Radiation

Since these Au atoms are produced from a hot source that is line-of-sight to the detector, the fraction of the heat signal due to optical radiation must be subtracted from the total signal. This contribution is measured by translating a BaF₂ flag into the beam path prior to and following calorimetry, which blocks all of the metal atoms, but transmits >90% of the radiation. The precise transmission of this BaF₂ flag is measured before and after each experiment with the HeNe laser using the procedure described above.

2.5.3 Flux Measurements

The absolute flux of Au atoms in each pulse was measured using a calibrated QCM that translates into the sample position (along the central axis of the atomic beam) before and after each calorimetry experiment. A second off-axis QCM monitors the flux of metal atoms during the entire duration of the experiment. It has been shown previously that the ratio between the flux measured at these two QCMs changes linearly with time within the duration of these experiments,⁷³ which will be discussed in further detail below. Therefore, by measuring the initial and final flux ratios between these two QCMs, the flux at the monitor QCM can be scaled to provide the flux at the sample position during heat measurements.

2.5.4 Sticking Probability

The sticking probability was measured using a modified King-Wells method,⁸⁹ using a line-of-sight QMS to measure the fraction of Au atoms that transiently adsorb to the surface but do not stick permanently. This QMS signal is compared to a reference zero sticking pulse from a hot Ta flag (1800-2000 K), which is located at the same position as the sample and corrected for average velocity.

2.5.5 Conversion to Standard Enthalpy

To convert the calorimetrically measured internal energy changes into standard enthalpy changes at the sample temperature (300 K or 100 K), the excess translational energy of the Au gas atoms at the oven temperature above that for a Maxwell-Boltzmann distribution at the surface temperature was subtracted, and a small pressure-volume work term (RT per mole) was added, as described elsewhere.^{72,90} In brief, for an ideal gas, Comsa and David⁹⁰ showed that the average

kinetic energy of an effusive molecular beam is $4/2 k_B T$ compared to $3/2 k_B T$ for a Boltzmann distribution. Thus adsorption energy is given by:

$$E_{\text{ads}} = -\Delta U = q_{\text{cal}} - (4/2 RT_{\text{source}} - 3/2 RT_{\text{sample}}) \quad (2.1)$$

where U is the internal energy and q_{cal} is the measured calorimetric heat.⁷²

2.6 IMPROVEMENTS ON PREVIOUS INSTRUMENTS

2.6.1 The e-Beam Evaporator Metal Atom Source

The most significant improvement to the newest calorimeter involves the method for generating the pulsed atomic beam of metal atoms. The SCAC measurements require a very high flux from a source located far from the sample in order to reduce optical radiation from the oven. Typical fluxes are 4×10^{14} atoms/cm²/s at the sample, which corresponds to $>4 \times 10^{17}$ atoms/cm²/s at the source, which is located 353 mm away. The original metal atom adsorption microcalorimeter design uses a Knudsen cell type thermal evaporator as the metal atom source.⁷² In the Knudsen cell, the entire metal crucible is heated to the temperature required to evaporate or sublimate the metal of interest. However, heating this large element to the high temperatures (upwards of 1660 K for evaporating Cu for example) required for the very high fluxes necessary in our calorimetry experiments produced too much background radiation. This background radiation contributes significantly to the measured heat signal, and it therefore proved unsuitable for studying metals with larger enthalpies of vaporization than that of Cu. The excessive heat load from the Knudsen cell also causes problems with background pressure increase for such metals, which can give rise to surface impurities.

To overcome this issue, the new instrument incorporates a Thermionics 150-0010 crucible-fed electron beam evaporator as the source for the metal atom beam. Its 4 kV electrons are focused

directly onto the surface of the metal to be evaporated, thereby localizing the heating to the metal itself. The metal to be evaporated is electrically grounded so that there is no difference in potential between the metal source and the single crystal, thus preventing acceleration of any charged species from the source to the sample. Electron beam evaporation allows for a significant flux of evaporated metals with a significant reduction in the heat and source radiation output when compared to a traditional Knudsen cell. This improvement has allowed us to use this new calorimeter with Au – which will be the focus of most of this work presented here – and Pt – which will be the focus of immediate future work.

2.6.2 Real-Time Flux Determination in the Metal Atom Beam

In order to analyze the calorimetry data, the flux of the metal atoms colliding with the sample surface must be known at all times. In previous calorimeter designs for SCAC, this was accomplished by measuring the flux before and after the experiment to prove that it had been stable during the calorimetry measurements.^{62,72,91} However, this requires a stable beam flux be maintained, which is more difficult to accomplish with metals with high vaporization enthalpies, as desired here. The stabilization of the metal flux of an e-beam evaporator can often be accomplished by controlling the e-beam emission current with feedback loops which monitor the ion current associated with the $\approx 1\%$ of metal atoms that are ionized by the e-beam evaporator. However, with the high fluxes required here, sudden changes in the shape of the melt caused large instabilities in the flux which could not be overcome.

Therefore, instead of controlling the metal flux, this technique incorporates a scheme to measure the real-time flux at the sample position based on the flux at a second monitor QCM (seen in Figure 2.1), which can be recorded simultaneously with the calorimetry data. This off-axis monitor QCM is located 225 mm from the metal source (compared to 353 mm to the sample) at a

70° angle from the atomic beam path to the sample to track the flux at all times during the calorimetry experiments. The ratio between the fluxes of the two QCMs is measured before and after the calorimetry experiments, and this ratio typically increases or decreases linearly as the flux decreases over time when the evaporator is run at constant emission current.

An example of a typical procedure using Cu is illustrated in Figure 2.2(a). At the beginning and the end of the experiment, the flux at both the monitor QCM and the sample position QCM are measured (shown as the data points) and the ratio between these two ranges is calculated. A linear fit between the initial and final ratio of the experimentally measured fluxes (the solid black line) is used to scale the flux at the monitor QCM so that it represents the actual flux at the sample position in real time over the entire duration of the calorimetry experiment (the solid red line). Proof that this ratio does in fact increase linearly with time while the source is being operated at constant emission current is shown in Figure 2.2(b) (provided the source has not used up almost all of its metal load).

Monitoring flux in real time in this way not only allows for more accurate calculations of heats of adsorption vs. coverage, but also allows us to use data sets in which there is a sudden shift in the flux of the metal atom beam, which can occur due to flow effects in the metal melt in the crucible and are especially problematic at high evaporation rates.⁹²

2.6.3 Optical Radiation from the Metal Atom Beam

When any metal evaporation source is used as a directed doser, as is the case in our calorimetry experiments, the atomic flux is also accompanied by optical radiation from the hot source. This contribution to the heat signal must be measured and subtracted from the signal in order to correctly determine the heat of adsorption.⁷² In our instrument, the source is located 353 mm from the sample and is collimated to a 4 mm diameter beam. This distance is necessary to

minimize the effect of the radiated heat from the oven, which decreases as the square of the distance. However, the flux per unit area from an effusion oven also decreases as the square of the distance. Because of this, very high temperatures in the source are required to reach the fluxes necessary for the signal/noise of our experiments (measured as a change in film thickness by the QCM of $\approx 0.5 \text{ \AA/s}$ at a 353 mm distance from the sample). Fortunately, the flux increases with temperature as an Arrhenius equation (proportional to $e^{-\Delta H_{\text{vap}}/RT}$, where ΔH_{vap} is the enthalpy of vaporization for molten metals) while the optical radiation increases only as ($\approx T^4$). For the enthalpies of vaporization of typical metals, the increase in flux is much faster than the increase in radiation, so that higher temperatures give larger fluxes and have a smaller contribution from optical radiation in this design.

In our original metal-atom source for SCAC of metal vapors, geometric constraints resulted in a situation in which the sample has direct line-of-sight to not only the metal melt in the thermal evaporator, but also to a portion of the heated crucible. In this new calorimeter, the source-to-sample distance was increased by 13%, and with this new geometry, the sample can now see only a 4.90 mm diameter portion of the metal source, which is substantially less than the $\approx 15 \text{ mm}$ diameter e-beam evaporator crucible.

The overall combined effect of the changes in geometry along with the new type of metal-atom source on the thermal radiation from the evaporative oven can be seen in Figure 2.3, where the voltage responses of the pyroelectric detectors to adsorption of gaseous Cu atoms on $\approx 17 \text{ ML}$ of Cu on $\approx 1 \text{ }\mu\text{m}$ single crystals are shown as black lines for the different experimental setups. One monolayer (ML) here is defined as the Cu(111) surface density of $1.77 \times 10^{15} \text{ atoms/cm}^2$. The solid blue lines are the corresponding optical radiation component in each pulse measured through the BaF₂ window, where these values have been scaled by the inverse of the measured transmission

of BaF₂ ($\approx 90\%$). The difference in the two solid lines is proportional to the heat response from only the adsorption of the gaseous metal atoms, and is plotted as a dashed red line to which the other data is normalized.

In Figure 2.3(a), the signal for 0.014 ML Cu pulses (which correspond to a flux of ≈ 0.3 Å/s at the sample in our systems with the Cu melt at 1500 to 1510 K) adsorbing onto 17 ML of Cu on a ≈ 4 nm MgO(100) film on Mo(100) from our older calorimeter using a Knudsen cell are shown.⁷² As seen, the optical radiation accounts for $\approx 65\%$ of the total heat signal. In Figure 2.3(b), the signal for 0.014 ML Cu pulses adsorbing onto 17 ML of Cu on Pt(111) in this new calorimeter using an e-beam evaporator are plotted in the same manner. In this case, the optical radiation is reduced to only $\approx 14\%$ of the total signal, which greatly improves the signal/noise ratio in the final heat of adsorption determinations. Since the Cu source was almost the same distance from the sample in these two cases (it is 7% longer in this new design), and the Cu flux is the same, the effective temperature of the Cu source (which defines the evaporation rate) was almost the same, but the new e-beam source clearly generates much less optical radiation at the detector. The difference in the line shapes between the two instruments is merely due to the use of a different time constant for the high-pass filter.

It should be noted that some of this apparent improvement is probably due to the difference in reflectivity of the samples. However, based on the reflectivities of Mo ($R \approx 0.57$ ⁹³) and Pt ($R \approx 0.76$ ⁹⁴), the maximum reduction in absorbance of optical radiation for the sample used in the e-beam evaporator (compared to that in the Knudsen cell experiment) would be 44%. Instead, a reduction in the absorbed optical radiation of 92% was observed. This proves that there is a minimum 51% reduction in optical radiation reaching the sample with our new calorimeter using an e-beam evaporator. It is likely that this improvement is even greater considering that the

reflectivities of the two samples should be approaching that of bulk Cu as the metal coverage increases. However, this may not be entirely due to the difference in the metal sources, as it is impossible to rule out a contribution from decreased internal reflections in the atomic-beam path due to improvements in the design of the light baffles.

Since this new metal-atom beam is capable of easily generating much larger fluxes of gaseous metal atoms without any significant rise in the background pressure, and since the atomic flux increases with temperature much faster than the optical radiation flux, the ratio between the radiative and adsorption heats can be further improved as needed. Figure 2.3(c) shows heat pulses from the same instrument onto the same sample used in Figure 2.3(b), but the flux has been increased by a factor of ≈ 4 to 0.058 ML per pulse (an increase in film thickness of $\approx 1.2 \text{ \AA/s}$ at the sample). In order to achieve this larger flux, the temperature of the melt was increased to 1600 K by increasing the emission current of the e-beam evaporator. This results in a decrease in the optical radiation with respect to the total heat signal, so that the optical radiation now only accounts for 7% of the total heat signal. This high-temperature capability allows us to use this atomic beam to perform adsorption calorimetry measurements with metals that have higher enthalpies of vaporization than Cu, such as Au and Pt.

2.7 FIGURES

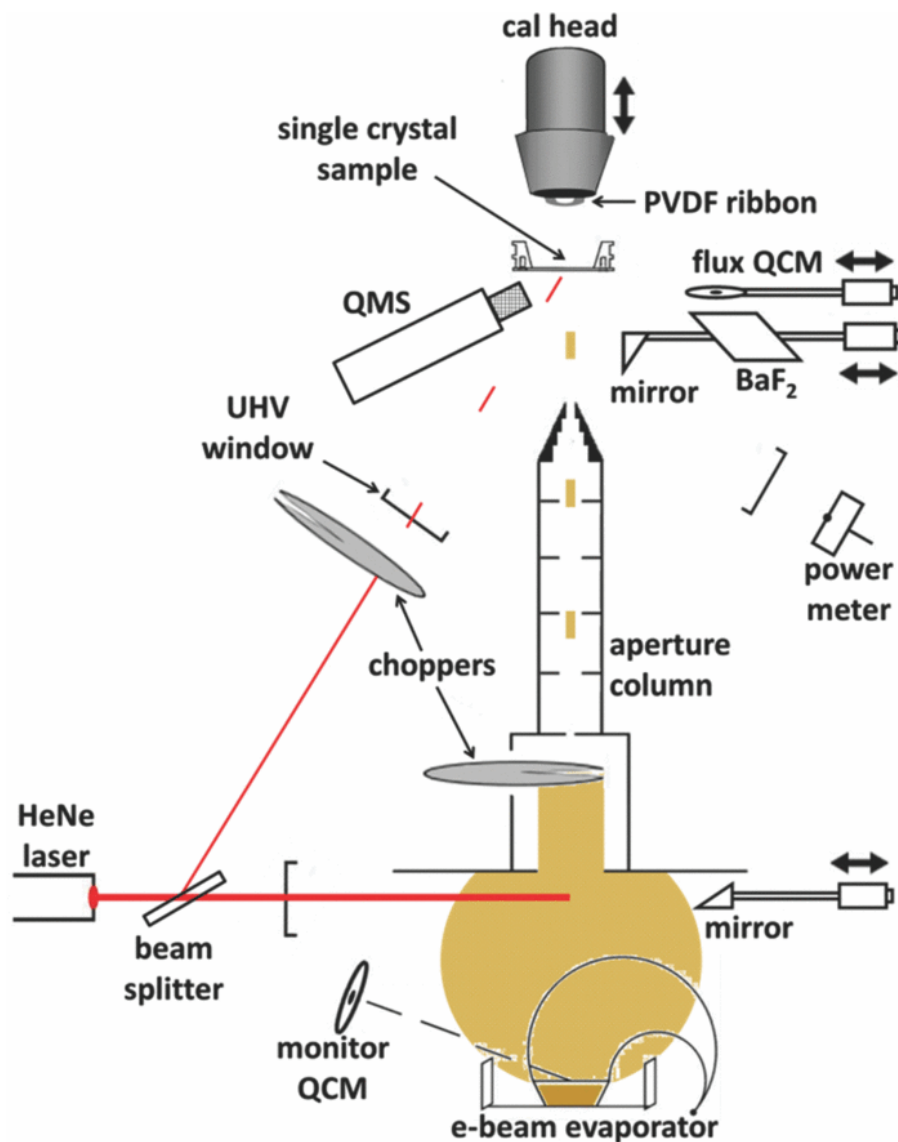


Figure 2.1. A schematic of the calorimeter, which uses an e-beam evaporator and a chopper to create a pulsed atomic beam of gaseous metal atoms (copper colored in the figure) which impinges upon the surface of a single crystalline sample. The transient heat input due to the adsorption of each gas pulse is detected by a flexible pyroelectric PVDF ribbon that is gently pressed against the back of the single crystal. As shown, this ribbon is mounted in the shape of an arch on the “cal head”, which can be translated to bring the ribbon into contact with the single crystal, or removed for crystal cleaning and surface analysis. The single crystal is mounted to a platen, which sits on a fork on a thermal reservoir during calorimetry but is moved for surface analysis. Also illustrated are the components for the real-time flux and relative reflectivity measurements. Not to scale.

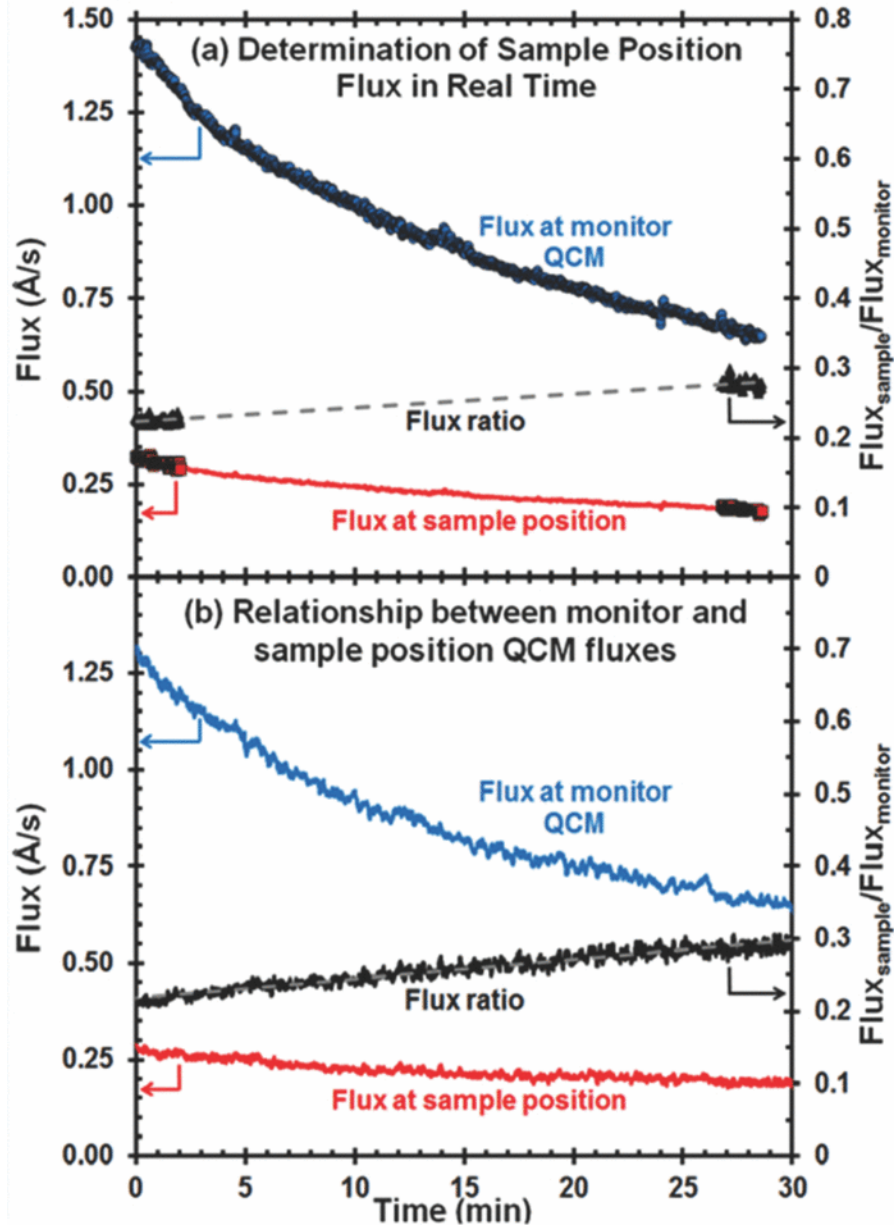


Figure 2.2. (a) Plot of the flux from the electron beam evaporator running at constant emission current vs. time at both the sample position QCM and the off-axis monitor QCM. Measured flux data are plotted as points, while the calculated flux at the sample position is plotted as a continuous red line. Also plotted is the ratio between the two fluxes, which is fit to the linear dashed line as a function of time. The flux ratio is used to calculate the flux at the sample position based on the flux at the monitor QCM. (b) Similar data for a control run where the flux was collected with a QCM located at the sample position throughout the entire experiment. This shows that the changing flux ratio is well approximated as changing linearly with time. The dashed line showing the best linear fit to the flux ratio is essentially hidden within the scatter of the data.

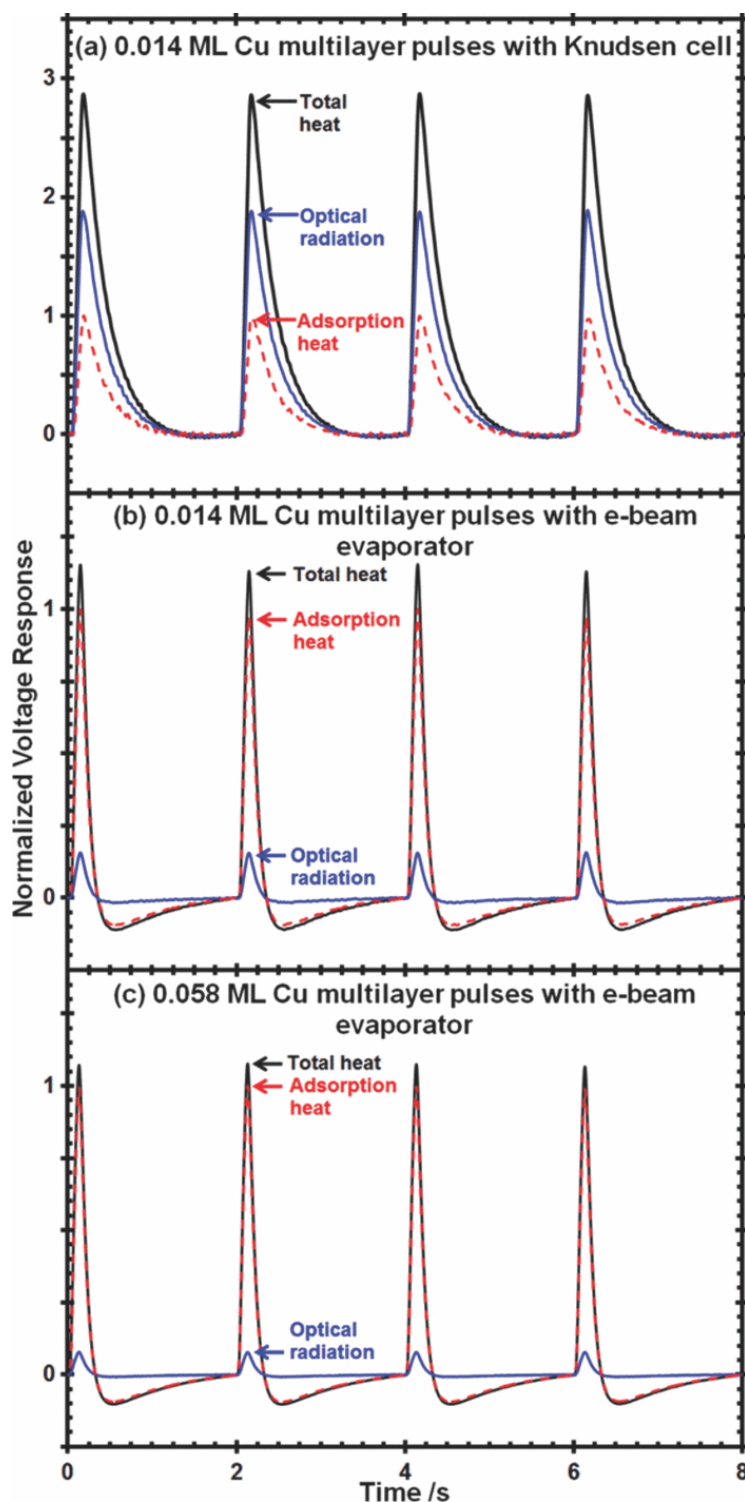


Figure 2.3. Calorimetry heat pulses as detected via SCAC from Cu adsorbing onto ≈ 17 ML of Cu on $\approx 1 \mu\text{m}$ single crystals at 300 K, where the Cu vapor was generated by: (a) the Knudsen cell used in our earlier calorimeter,⁷² and (b) and (c) the e-beam evaporator of this new instrument. The solid black lines are calorimetry data from Cu atom pulses, the solid blue lines are the heat due to optical radiation from the hot metal source (measured through the BaF₂ window at the end of the experiment) and the dashed red lines are the heat signal due only to Cu adsorption, as determined by the difference in the two solid curves. These signals are for (a) 0.014 ML pulses of Cu from the Knudsen cell used in our earlier calorimeter onto ≈ 17 ML Cu on Mo(100) (pre-coated with 4 nm of MgO(100), which only slightly changes the reflectivity⁷⁴), (b) 0.014 ML pulses of Cu from the e-beam evaporator onto ≈ 17 ML of Cu on Pt(111), and (c) 0.056 ML pulses of Cu from the e-beam evaporator onto

≈ 17 ML of Cu on Pt(111). The differences in line shapes arise from differing time constants for the high-pass filters and differences in the quality of the sample – detector thermal contact. Curves were smoothed with a low-pass filter. One ML is defined as the Cu(111) surface atom density, 1.77×10^{15} atoms/cm².

Chapter 3. Adsorption and Adhesion of Au on Reduced CeO₂(111) Surfaces at 300 and 100 K

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The adsorption of vapor-deposited Au onto CeO_{2-x}(111) thin films ($x = 0.05$ and 0.2) at 300 K and 100 K was studied using single-crystal adsorption calorimetry (SCAC). The morphology of Au on these films was investigated using He⁺ low-energy ion scattering spectroscopy (LEIS) and X-ray photoelectron spectroscopy (XPS) by monitoring the changes in substrate and adsorbate signals with Au coverage. Both techniques indicate that Au grows on CeO_{1.95}(111) as three-dimensional particles in the approximate shape of hemispherical caps with a density of 2.8×10^{12} particles/cm² at 300 K and 7.8×10^{12} particles/cm² at 100 K. At 300 K, Au initially grows on CeO_{1.80}(111) with a shape similar to hemispherical caps with a density of 5.4×10^{12} particles/cm² until ≈ 1.6 ML Au coverage, above which the Au particles become thicker than hemispherical caps. At 300 K, the initial heat of adsorption of Au onto CeO_{1.95}(111) is 259 kJ/mol, which is 37 kJ/mol lower than on CeO_{1.80}(111). This indicates stronger binding of Au to oxygen vacancies. On both surfaces, the Au heats of adsorption increase slowly with coverage, approaching the bulk heat of sublimation of Au(solid) (368 kJ/mol) by ≈ 2 ML (3.2 nm in diameter on CeO_{1.95}(111), 2.4 nm on CeO_{1.80}(111)). The heat of adsorption remains higher on the reduced surface than on the oxidized surface at all particle sizes. At 100 K, the initial heat of Au adsorption onto CeO_{1.95}(111) is 209 kJ/mol (50 kJ/mol lower than at 300 K), which is due to a higher fraction of Au atoms adsorbing to terraces compared to step sites. The adhesion energy of Au(solid) to

CeO_{1.95}(111) at 300 K was found to be 2.53 J/m² for 3.6 nm diameter particles, and 2.83 J/m² onto CeO_{1.80}(111) for 2.5 nm diameter particles. This further indicates that Au particles bind more strongly to surfaces with a larger fraction of oxygen vacancies.

3.1 INTRODUCTION

The properties of transition metal nanoparticles supported on oxides can vary dramatically with nanoparticle size between 1-10 nm,⁹⁻¹¹ and some metals that are relatively inert in the bulk, especially gold, can become highly active at this scale for a variety of catalytic reactions.^{13,15,16,25} These variations in reactivity with particle size have been correlated with the energy or chemical potential of the metal atoms in the particles.⁵⁶ Supported gold nanoparticles have shown high activity as catalysts for combustion and selective oxidation reactions,^{13,43,95} and ceria is often used as the support material.^{50,96-101} Thus, Au nanoparticles on ceria have been extensively studied both by a variety of experimental methods¹⁰²⁻¹⁰⁸ as well as by DFT.^{31,32,108-118} In this chapter, the first experimental measurements of the energies of gold atoms in supported gold nanoparticles are reported as a function of their size. This is done for the case of CeO₂(111) support surfaces with different extents of reduction.

Gold displays the most dramatic size-dependent properties of any of the late transition metals.²⁵ Because of this strong size dependence, stabilizing gold nanoparticles at their optimum size is critical. However – as for most late transition metals – the bulk phase is more thermodynamically stable than highly dispersed nanoparticles, and the excess of under-coordinated surface atoms on small particles drives them to agglomerate and form larger particles over time.^{34,35} This particle coarsening process is the primary cause of catalyst deactivation in these types of materials,³⁷ and it is particularly problematic in the case of supported gold nanoparticles due to gold's strong tendency to coarsen and its size-dependent melting temperature.¹¹⁹

The choice of support can dramatically affect the catalytic properties of the system such as activity and selectivity.^{13,46,47} When supported on ceria, gold nanoparticles have shown to be effective for several critical catalytic reactions such as the water-gas shift reaction, the combustion of organic compounds,⁹⁹ and low-temperature CO oxidation.⁹⁵ Ceria by itself is also a good catalytic material for methane combustion, methanol synthesis, and the water-gas shift reaction.^{50,120} Its utility derives partly from its ability to exchange oxygen with its environment due to its facile reducibility, which stems from the nearly equal stability of its two oxidation states (CeO_2 and Ce_2O_3). When oxygen atoms are removed from CeO_2 , they leave behind negatively charged vacancies that reduce nearby Ce^{4+} atoms to Ce^{3+} .^{121,122} As a support, ceria dramatically enhances the catalytic activity of a variety of metals for catalytic reactions such as CO oxidation,^{101,102} NO reduction,¹²³ and H_2 production.⁹⁸

Ceria is also known to maintain smaller metal nanoparticles and resist particle coarsening better than other oxide supports.^{41,50,124} In a recent study of Ag adsorption on $\text{CeO}_{2-x}(111)$, it was observed that for small average particle sizes (< 4 nm), Ag binds to $\text{CeO}_{2-x}(111)$ with higher heats of adsorption than to $\text{MgO}(100)$.³⁹ This strong metal binding explains why ceria helps maintain smaller nanoparticles. It was also found that the heat of adsorption is higher for a more reduced ceria surface, suggesting that oxygen vacancies are favorable for coarsening resistance due to stronger Ag binding, which had been proposed by density functional theory (DFT).³¹ However the kinetics of deactivation – as well as the dependence of catalytic properties on the physical and chemical properties of the metal and support – remain difficult to elucidate. It has been shown that sintering kinetics correlate with the size-dependent energies of metal atoms in particles.^{33,35,57,125} This is because the thermodynamic driving force for sintering results from the difference between the internal energy of a metal atom in a nanoparticle on a surface and the energy of metal atoms in

the bulk. Therefore, the ability to measure the energy of metal atoms in supported nanoparticles and the corresponding metal / support adhesion energies is crucial for understanding sintering and its inhibition. The measurements presented here for these energies of Au on CeO_{2-x}(111) will help elucidate gold sintering rates.

Particle size-dependent gold atom adsorption and gold nanoparticle adhesion energies on CeO_{2-x}(111) are measured here using single-crystal adsorption calorimetry (SCAC), an ultrahigh vacuum (UHV) technique which allows full control of surface cleanliness. This technique utilizes a highly sensitive detector to measure minute temperature changes upon the adsorption of metal atoms on single-crystal oxide substrates. SCAC has been used for a variety of metal / oxide systems to directly measure the energy of metal atoms as they bind to the oxide surface, and to nanoparticles as they continue to grow.^{39,56,57,64} These measurements are supported by low-energy ion scattering spectroscopy (LEIS) and X-ray photoelectron spectroscopy (XPS) to monitor the growth and morphology of metals deposited on oxides. By combining the adsorption energies with detailed information of particle morphology and growth, nanoparticle adhesion energies are determined. These adhesion energies are compared to gold particle adhesion energies on MgO(100) and CeO₂(111) measured using particle shape measurements with electron microscopy.^{76,105}

Because of its importance in catalysis, the adsorption of gold onto both stoichiometric and reduced CeO₂(111) surfaces has also been studied extensively by DFT with periodic boundary conditions.^{31,32,108–118} These gave adsorption energies for Au monomers on the most stable terrace sites of stoichiometric CeO₂(111) ranging from 59 to 122 kJ/mol depending on the DFT method. There is a strong consensus in DFT that gold adatoms are stabilized by both surface and subsurface oxygen vacancies.^{108–117}

To our knowledge, no experimental measurements of the adsorption energy or strength of Au interfacial bonding to any clean ceria surface have been reported previously. The calorimetric measurements presented here of the adsorption and adhesion energies of Au onto CeO₂(111) is the third such investigation of metal adsorption onto reduced CeO₂(111) surfaces, after our previous reports for Ag^{39,70} and Cu.^{126,127}

3.2 EXPERIMENTAL DETAILS

The CeO_{2-x}(111) thin films were grown on Pt(111) as described in detail previously^{70,126} in an adjacent UHV preparation chamber. The Pt(111) surface was cleaned by successive cycles of 1 kV Ar⁺ sputtering in 6 x 10⁻⁶ Torr Ar followed by annealing to 1173 K in UHV followed by 873 K in 1 x 10⁻⁶ Torr O₂ until no C was present in XPS and a sharp Pt(111) LEED pattern was observed. The CeO_{2-x}(111) films were grown via reactive evaporation of Ce in a 1 x 10⁻⁶ Torr O₂ background gas at a sample temperature of 873 K, and the as-grown films were then annealed at 873 K in this same background pressure of oxygen for 5 minutes. The average CeO₂ deposition rate was 0.4 nm/min as determined by the attenuation of the Pt 4p_{3/2} photoelectron peak, using the inelastic mean free path of Pt 4p_{3/2} electrons escaping through CeO₂ calculated using NIST inelastic mean free path database (17.5 Å). The oxidation state of the ceria films was determined by XPS (see below) and sample order was verified by LEED. Reduced CeO_{1.80}(111) samples were grown using the same procedure but with a reduced oxygen pressure of 1 x 10⁻⁷ Torr and a reduced annealing time of 0.5-2 minutes. Before each calorimetry measurement, the detector was retracted and the surface was flash-heated to 873 K (measured by optical pyrometry) in 1 x 10⁻⁶ Torr O₂ to remove any adsorbed background gases.

3.3 RESULTS

3.3.1 CeO_{2-x}(111) Thin Film Characterization.

Thin films of CeO_{2-x}(111) (where $x = 0.05$ and 0.2) were grown in the connected UHV preparation chamber to a thickness of 4-6 nm on a 1 μm thick Pt(111) substrate as described previously.¹²⁶ This was thick enough to give bulk-like ceria surface properties, since it has been shown that 2-3 nm thick CeO_{2-x}(111) films have the same Ag atom adsorption energies as 4 nm thick films, while 1 nm thick films bind Ag more strongly.⁷⁰ The (111) surface order was verified by LEED, which gave a sharp (1 x 1) pattern. The CeO_{2-x}(111) film thickness was calculated by the attenuation of the Pt 4p_{3/2} peak in XPS. The oxidation state of these ceria films was determined from the relative contributions of Ce³⁺ and Ce⁴⁺ to the Ce 3d region in XPS (see Ref. ¹²⁶ and ¹²⁸). A detailed description of CeO₂(111) film growth can be found in Refs. 70 and ¹²⁶.

3.3.2 Au Sticking Probability on CeO_{2-x}(111).

The sticking probability of Au atoms onto CeO_{2-x}(111) as a function of total Au coverage was calculated by monitoring the number of non-sticking Au atoms in each pulse. This was measured as previously⁷² by comparing the magnitude of the time-integrated transient QMS signal for Au vapor during each calorimetry pulse to a zero-sticking reference signal that was generated by placing a hot Ta foil flag in the sample position and resistively heating it so all incoming Au atoms rapidly desorb. The measured sticking probability was >0.98 at all Au coverages on both the oxidized ($x = 0.05$) and reduced ($x = 0.2$) ceria films at both 300 K and 100 K.

3.3.3 Au Morphology on CeO_{2-x}(111) at 300 K.

The Au nanoparticle morphology on CeO_{2-x}(111) at 300 K was tracked with He⁺ LEIS with increasing Au coverage, as shown in Figure 3.1. Au coverages are given throughout in units of

ML, defined as the number of oxygen atoms per unit area in the topmost atomic plane of CeO₂(111). Discreet quantities of Au were deposited using similar dose rates as those are used during calorimetry. Both the attenuation of the Ce substrate signal and the growth of the Au adsorbate signal were monitored as a function of total Au coverage. The integrated Ce peak areas were normalized to the signal from the clean ceria film prior to Au deposition, and integrated Au areas were normalized to a thick, bulk-like continuous Au overlayer (>60 ML). Since LEIS is sensitive only to the topmost atomic layer, the Au and Ce signal represent a direct measurement of the fraction of the ceria surface that is masked or unmasked by Au nanoparticles.¹²⁹ The data in Figure 3.1 are compared to both the layer-by-layer growth model and the hemispherical cap growth model described by Diebold et al.,¹³⁰ and later modified to better describe the macroscopic shadowing effects of hemispherical particles.¹³¹ This model has been shown to describe the morphology of many oxide-supported late-transition metals relevant to catalysis.⁴² In the case of Au (Figure 3.1 and Figure 3.2) the data deviate markedly from the layer-by-layer model, indicating that Au does not grow two-dimensionally at any coverage (except possibly below the lowest-coverage data point shown here at ≈ 0.25 ML).

The hemispherical-cap model assumes that the adsorbate film grows as 3D particles in the shape of hemispheres, and that these particles grow in size only while their number density, n , remains fixed at all Au coverages. Gold nanoparticles on CeO₂(111) have been observed to have nearly hemispherical particle shapes at 300 K in the STM work of Lu et al.¹⁰² as well as in several TEM studies.^{103,132} In our system, the angle of LEIS detection is normal to the surface and the incident He⁺ ion beam is at an angle $\theta_i = 45^\circ$ from the surface normal. Using these parameters, the fraction of the ceria substrate signal masked by Au particles is given as $n\pi D^2 (1+1/\cos\theta_i)/8$ where D is the average diameter of the particles. Since the total Au coverage is known at each point, and

must be equal to $n(4/3)\pi D^3$ divided by the atomic volume of Au(solid), the number density n then becomes the only fitting parameter. Its best-fit value is then used with the Au coverage to calculate D at each Au coverage point.

As in the case of previously studied noble metals, the data on CeO_{1.95}(111) are well fit using this modified hemispherical-cap model.^{67,126,129} Using a least-squares analysis gave a Au particle density for deposition at 300 K of 2.8×10^{12} particles/cm² on the oxidized surface and 5.4×10^{12} particles/cm² on the reduced surface (nearly two times larger). The data were fit up to $\approx 35\%$ total Au surface coverage, at which point this model breaks down because particles may begin to overlap. Above this 35% threshold, which occurs at ≈ 1.7 -1.8 ML total Au coverage, the Au and Ce signals on the oxidized surface continue to track the hemispherical-cap model, while on the reduced surface the Au and Ce signals stop changing above 1.6 ML. This “saturation” in signal indicates that the particles are getting thicker than hemispherical caps, which will be described in detail in the discussion.

A more direct way to represent the morphological implications of these data that requires no assumption of particle shape is to replot them to show the average particle thickness as a function of total Au deposited. The normalized LEIS signal shown in Figure 3.1 directly measures the fraction of the ceria surface that is masked by Au particles at any given Au coverage. By assuming that the footprint of the Au particles is expanded due to macroscopic shadowing by approximately the same factor as in the case for hemispherical caps at the given analysis geometry ($((1 + 1/\cos\theta_i)/2 = 1.207)$,¹³¹ these values can be divided by 1.207 to estimate the real fractional area that is covered by Au particles. (This value of 1.207 is a minor correction factor that depends only weakly on particle shape; e.g., it would be 1.0 for 2D islands.) The average Au film thickness equals the total Au coverage multiplied by the atomic volume of bulk Au(solid). Dividing this

average thickness by the fractional area as measured by each LEIS data point (both from the Au and Ce normalized signal) gives the average Au particle thickness.^{126,131} Figure 3.2 shows the same data as in Figure 3.1 presented as the average Au particle thickness as a function of total Au deposited for both the oxidized and reduced ceria films at 300 K estimated as described above. Additionally, since the average thickness of a hemispherical cap is 1/3 its diameter, this thickness is multiplied by 3 on the right-hand axis to show the corresponding average particle diameter, assuming hemispherical shape. The result expected from the same hemispherical-cap model and best-fit particle number density from Figure 3.1 is shown for reference, and agrees well with the data on the oxidized surface at all coverages, as well as for the reduced system below ≈ 1.6 ML. When presented in this way, it is clear that the average particle thickness grows more rapidly than would be expected for the hemispherical-cap model above 1.6 ML, suggesting that these particles deviate from the hemispherical cap shape and begin to grow with a thicker aspect ratio than hemispherical caps. Gold particles that are thicker than hemispherical caps have been observed by TEM after growth at 300 K at CeO₂(111) and bombardment with electrons to create oxygen vacancies.¹³³

To ensure that no significant ion damage was done to the sample by He⁺ ion bombardment during the LEIS experiments in Figure 3.1, control experiments were done in each case using only four coverage points: 0 ML, 1 ML, 4 ML, and >60 ML. The zero and “full” coverage points are used for normalization, and the two intermediate points were chosen at signals that are still highly sensitive to small changes in coverage. This procedure resulted in four-fold less total ion beam exposure at those points, yet the data from these experiments fell within error of the best-fit lines for each sample in Figure 3.1. This indicates that He⁺ ion beam damage did not significantly affect these results.

3.3.4 Au Morphology on CeO_{2-x}(111) at 100 K Using LEIS.

The same LEIS measurements as described above for the surface at 300 K were used to monitor the morphology of Au on these same two ceria surfaces at 100 K, in order to investigate the effects of reduced Au adatom mobility at lower temperatures. The data for CeO_{1.95}(111) at 100 K are shown in Figure 3.3 along with the data at 300 K for comparison. The best-fit Au particle density on CeO_{1.95}(111) at 100 K was found to be 7.8×10^{12} particles/cm², which is roughly a three-fold increase from the value at 300 K. The resulting comparison between this system at 300 K in average particle thickness (and effective diameter) versus coverage is shown in Figure 3.4, analyzed using the same logic described above. Clearly, the Au particles on CeO_{1.95}(111) are thinner (flatter) at 100 K than at 300 K, consistent with this 3x larger particle number density.

Similar LEIS data versus coverage was collected on CeO_{1.80}(111) at 100 K, but is not presented here, since it was qualitatively very similar to Au on CeO_{1.95}(111) at 100 K, and the best-fit particle density was nearly the same (8.9×10^{12} particles/cm²). This is less than two times larger than at 300 K. The increase in particle density from the oxidized to the reduced ceria surface at 100 K is also much smaller than at 300 K. This suggests that the saturation density at 100 K on both surfaces is much closer to that predicted for homogeneous nucleation models¹³⁴ (as opposed to a density determined by the defect density). Since homogeneous nucleation results in higher densities at lower temperatures, it is expected that it will occur at low temperatures even for systems where defect-defined density occurs at higher temperatures.¹³⁴ It was observed that the Au and Ce LEIS signals versus Au coverage on CeO_{1.80}(111) at 100 K did *not* “saturate” at high coverage, as they did at 300 K (Figure 3.1), but instead track the hemispherical-cap model quite well at all coverages (not shown).

Consistent with these LEIS results, Au particles have been observed to grow with a shape similar to hemispherical caps on $\text{CeO}_{2-x}(111)$ at temperatures as low as 100 K in both STM¹⁰² and TEM.^{106,132,133} Even when Au is deposited at 10 K onto $\text{CeO}_{1.95}(111)$ 3D clusters of two or more Au atoms are observed along with individual Au monomers.¹³⁵ It is known that gold particles orient themselves onto the $\text{CeO}_2(111)$ facets of polycrystalline ceria with their Au(111) planes preferentially parallel to the $\text{CeO}_2(111)$ plane, in spite of the bulk lattice mismatch of 28% between these surfaces.^{105,132}

3.3.5 Au Morphology on $\text{CeO}_{2-x}(111)$ Using XPS

The morphology of Au on $\text{CeO}_{1.95}(111)$ and $\text{CeO}_{1.80}(111)$ at 300 K as well as the morphology of Au on $\text{CeO}_{1.95}(111)$ at 100 K were also studied using XPS as shown in Figure 3.5. The integrated intensities of the Au 4f_{5/2} and Ce 3d XPS regions were normalized using the same coverages as the LEIS signals as described above, and are plotted versus total Au coverage. Each individual system shown here is the average of 2 or 3 runs. The Au data were fit using the literature value for the electron inelastic mean free path at a kinetic energy of 1409 eV (1.66 nm¹³⁶) and the Ce data were fit using a value of 0.9 nm, which was the value determined as the best-fit mean free path for Ce 3d electrons at a kinetic 580 eV escaping through a Au overlayer based on a particle density determined by LEIS.^{126,130} As was done previously for Cu/ $\text{CeO}_{2-x}(111)$, this value was chosen instead of the literature value of 1.14 nm due to forward focusing of the electrons through an ordered lattice.¹³⁶ Because XPS is far less surface sensitive than LEIS, it is not as powerful in revealing morphology, but these results in Figure 3.5 further support the conclusions from LEIS, and confirm that the system does not grow in a layer-by-layer fashion.

3.3.6 Heat of Adsorption, Adhesion of Au on CeO_{2-x}(111) at 300 K and 100 K

The calorimetric heats of Au atom adsorption onto CeO_{2-x}(111) (for $x = 0.05$ and 0.2) at 300 K and for $x = 0.05$ at 100 K are shown as a function of Au coverage in ML in Figure 3.6. All heats of adsorption here have been corrected for the small translational energy difference between incident atoms from the hot surface of the metal atom source and these same atoms in a Boltzmann distribution at the sample temperature (either 300 K or 100 K) as described previously.⁷² By doing so, these data correspond to the standard enthalpy of adsorption with both the gas and the solid at the temperature of the ceria film (multiplied by negative one, so that exothermic values are presented here as positive rather than negative, as is conventional in calorimetry).

At 300 K, the initial heat of adsorption of Au on CeO_{1.80}(111) (296 kJ/mol) is 37 kJ/mol larger than the initial heat on CeO_{1.95}(111) (259 kJ/mol). As coverage increases, the Au heat of adsorption increases at a qualitatively similar rate on both surfaces due to the formation of more Au-Au bonds per adatom as the particle diameter grows (see below). However, the heat of adsorption remains higher on the reduced surface than on the oxidized surface at all coverages until ≈ 2 ML, above which both systems reach the bulk heat of sublimation of Au(solid) (368 kJ/mol at 300 K¹⁸). Similar behavior was observed for Ag on CeO_{2-x}(111), and this difference was attributed to stronger binding at oxygen vacancy sites, which have a higher number density on a more reduced ceria surface.⁷⁰ At 100 K, Au adsorbs on CeO_{1.95}(111) with an initial heat of adsorption of 209 kJ/mol (50 kJ/mol lower than at 300 K) and increases rapidly with coverage until ≈ 1.4 ML. Above this point, it is nearly flat until just above 3 ML, at which point it begins to increase towards the standard heat of sublimation of bulk Au(solid) (363 kJ/mol at 100 K¹⁸) which it reaches by ≈ 6 ML. The lower initial heat of adsorption of Au on CeO_{1.95}(111) at 100 K compared to 300 K is partially due to the formation of smaller particles at lower temperatures (see above),

but it is also likely due to a higher fraction of Au atoms adsorbing to terraces compared to step sites at 100 K due to slower diffusion of Au atoms. Generally, step sites are more energetically favorable than terrace sites for late transition metals adsorbing onto oxide surfaces^{42,137,138}, as shown also for Ag^{70,139} and Cu¹²⁶ onto CeO₂(111).

Using the relationship shown in Figure 3.2 and Figure 3.4 between Au coverage and average particle diameter (where the hemispherical-cap model holds), or the best-fit particle density determined in LEIS, Au coverage in ML can be converted into average Au particle diameter. In this way, the Au heat of adsorption can be replotted versus average Au particle diameter for each of the three systems (Au / CeO_{1.95}(111) at 300 K, Au / CeO_{1.80}(111) at 300 K (up to 1.6 ML), and Au / CeO_{1.95}(111) at 100 K), as show in Figure 3.7. When presented in this way, it is clear that for a given extent of reduction of ceria, the heat of adsorption correlates strongly with particle diameter, almost independently of surface temperature. Such an increase in heat with size has been reported for many metal-on-oxide systems,^{56,57} and is due to the increasing number of metal-metal bonds that are formed upon the addition of one metal atom to a larger particle. For example, a metal adatom can form at most three bonds to a trimer, whereas it makes (on average) six metal-metal nearest neighbor bonds upon adsorbing to a bulk FCC metal surface. The Au heat of adsorption reaches the Au bulk heat of sublimation for particles ≈ 3.2 nm in diameter on CeO_{1.95}(111), and ≈ 2.4 nm in diameter on CeO_{1.80}(111). In the case of Au adsorption on CeO_{1.95}(111) at 100 K, the first several (lowest coverage) points correspond to smaller particles than at 300 K. Therefore, the heat of adsorption for these smaller particle sizes is lower. For comparable small particle sizes, the heats are slightly higher at 300 K than at 100 K for the same particle size. This is attributed to the larger contribution from stronger binding to step sites, since faster diffusion allows incoming Au adatoms to find these favorable sites more frequently at 300

K than at 100 K. The heats at 100 K and 300 K converge at a particle diameter of ≈ 1.5 nm, and track each other above this point. The data at 100 K is only shown up to the coverage where 35% of the surface is covered by Au particles (see above), since the hemispherical-cap model can no longer be applied above that coverage.

The adhesion energy of nanoparticles onto a flat surface, E_{adhesion} , can be calculated from the integral heat of adsorption and measured morphology from LEIS using a thermodynamic cycle described in Ref. ⁴². This gives the following relationship:

$$n \sum_n \Delta H_{\text{ads}} = -n \Delta H_{\text{sub}} + A[(1 + f)\gamma_{\text{v/m}} - E_{\text{adh}}] \quad (3.1)$$

where $\gamma_{\text{v/m}}$ is the surface energy of the bulk nanoparticle material, f is the surface roughness factor ($f = 2$ for a hemispherical cap), $\sum_n \Delta H_{\text{ads}}$ is the integral (average) molar heat of adsorption up to the coverage (particle size) of interest, n is the number of moles of the adsorbate on the surface at that coverage, A is the total area covered by the metal nanoparticles, and ΔH_{sub} is the bulk heat of sublimation of the adsorbate. Using this method requires that the adhesion energy be calculated at coverages where the hemispherical-cap model is valid, since only there is the surface roughness factor known. To achieve this but also have the largest possible particles (to approach as closely as possible to the large-particle limit), this technique is applied to the highest coverage where no more than $\approx 35\%$ of the surface is covered by the adsorbate (as determined by LEIS). On the $\text{CeO}_{1.95}(111)$ surface, this corresponds to an Au coverage of 2.7 ML, or an average particle diameter of 3.6 nm. Using the integral heat at this coverage in the above equation gives an adhesion energy of 2.53 J/m^2 . On the reduced $\text{CeO}_{1.80}(111)$ surface, the adhesion energy is calculated at a coverage of 1.6 ML or an average particle diameter of 2.5 nm, and is 2.83 J/m^2 , which is larger than the value found for slightly larger particles on the more fully oxidized surface. This further

indicates that Au particles bind more strongly to surfaces with a larger fraction of oxygen vacancies.

3.4 DISCUSSION

3.4.1 Comparative Adsorption on Steps, Oxygen Vacancies, and Terraces

The $\text{CeO}_2(111)$ surface is oxygen terminated, and oxygen vacancies are expected to be the primary point defects rather than cerium vacancies.¹¹⁷ Partially reduced $\text{CeO}_{2-x}(111)$ films (with a higher density of oxygen vacancies) can be prepared by growing the oxide under reduced oxygen pressure,¹⁴⁰ by electron bombardment,¹⁴¹ or by post-growth high-temperature annealing.^{142,143} The method used here of growing and then annealing reduced ceria films in a lower oxygen pressure is similar to the process used by Lu *et. al* on $\text{Ru}(0001)$,¹⁰² which was modified from the original recipe of Mullins *et. al*,¹⁴⁴ and was observed to form wide, atomically flat terraces. Using arguments discussed in detail in Ref. ¹²⁶, our preparation method produces $\approx 5\%$ step sites on the $\text{CeO}_{1.95}(111)$ surface, with the oxygen vacancies located mainly at these steps (where they are far more stable than at terraces). The steps on the $\text{CeO}_{1.80}(111)$ surface are likely missing nearly all of their O atoms, with many oxygen vacancies present at other locations as well.

Preferential nucleation of Au particles and monomers at step edges has been observed on $\text{CeO}_2(111)$ with microscopy after deposition at – or warming to – 300 K.^{102,106,132,133} Most vapor-deposited late transition metals supported on single-crystal oxide surfaces have a strong energetic preference to nucleate particles at step edges compared to stoichiometric terraces, which has been attributed to stronger bonding at steps.^{42,59} However, the only prior direct experimental measurement of adsorption energies that confirms this is our earlier observation that the heat of Cu adsorption onto $\text{CeO}_{1.95}(111)$ to form Cu dimers is ≈ 60 kJ/mol higher at 300 K (where dimers are expected to nucleate at steps) than at 100 K (where they are diffusionally limited to form on

terraces).¹²⁷ The same effect is confirmed here, showing in Figure 3.7 that the heat of adsorption of Au onto CeO_{1.95}(111) at a Au particle diameter of ≈ 0.7 nm is ≈ 27 kJ/mol higher at 300 K (where step edges are surely the majority of the nucleation sites) than at 100 K (where nucleation also occurs on terraces due to slower Au diffusion). This difference is nearly equivalent to what was observed for Cu on CeO_{1.95}(111), where the heat of adsorption for ≈ 0.7 nm Cu particles at 300 K was found to be ≈ 30 kJ/mol higher than at 100 K. Since the oxygen vacancies are located mainly at step edges on this surface, this difference probably has two contributing factors: (1) intrinsically stronger binding of Au to step edges even at the same extent of reduction, and (2) intrinsically stronger binding of Au to oxygen vacancies.¹¹⁵ For Au on the fully-oxidized (stoichiometric) CeO₂(111) surface, monomers were predicted by DFT (LDA+U, U = 5 eV for geometry optimization, GGA+U, U = 3 eV for energies) to be ≈ 165 kJ/mol more stable at steps than on terrace sites.¹¹¹

It has also been predicted by numerous DFT studies^{111,112,116,117,145} and confirmed experimentally^{108,118,135,146} that Au binds more strongly to oxygen vacancies than to stoichiometric terraces. Here, for Au particles ≈ 0.7 nm in diameter, the heat of Au adsorption on CeO_{1.80}(111) is 37 kJ/mol higher than on CeO_{1.95}(111). Since Au particles are probably located mainly at step edges on CeO_{1.95}(111), while they are likely both at steps and terraces on CeO_{1.80}(111) (see below), this higher heat of adsorption likely results from the difference in Au binding between step edges with nearly 100% versus $\approx 50\%$ oxygen vacancies. However, since a large fraction of the particles are also probably located at oxygen vacancies on terraces on the more reduced surface (see below), to which Au probably bonds more weakly than at step edges with 50% vacancies, the actual difference between steps with 100% versus 50% oxygen vacancies may be larger than this 37 kJ/mol.

This raises the question of whether Au is energetically more stable at terrace oxygen vacancies or at steps with $\approx 50\%$ vacancies. Using STM, Lu et al.¹⁰² found that Au particles deposited at 300 K primarily occupied steps on stoichiometric $\text{CeO}_2(111)$. No surface oxygen vacancies were observed, however a small number of terrace sites were still populated by Au particles, which the authors attributed to the presence of subsurface vacancies or their agglomerates. When more reduced $\text{CeO}_{2-x}(111)$ films were prepared both by growing in reduced oxygen pressure¹⁰² and by thermal annealing,¹⁰⁷ Au particles were found to nucleate and grow primarily on terraces rather than steps at 300 K, which was accompanied by an increase in the particle density (roughly twice the number of surface oxygen vacancies, indicating that Au clusters nucleate not only at surface oxygen vacancies, but also near subsurface defects or other stoichiometric defects). This suggests that when surface oxygen vacancies are present, Au atoms bind more strongly to these defect sites than to steps, or alternatively that surface oxygen vacancies “trap” diffusing Au adatoms on terraces long enough to nucleate a particle. In other words, the appearance of more Au particles on terraces that have more oxygen vacancies could easily be a kinetic effect rather than a thermodynamic preference for oxygen vacancies over steps.^{102,107}

Theoretical studies may shed additional light on this question. However, modeling Au adsorption on $\text{CeO}_2(111)$ has proven to be exceptionally challenging, and has produced several contradictory results, many of which are summarized in two excellent reviews.^{32,115} These studies are based on Density Functional Theory, and it has been universally shown that this particular system is extremely sensitive to the choice in the exchange-correlation functional approximation. One observation that seems to be qualitatively agreed upon is that the adsorption energy of an Au atom at a surface oxygen vacancy is much higher than an Au atom on a stoichiometric terrace site (either on top of a surface oxygen or bridging between two). Given the previously discussed

assumption that both of our prepared $\text{CeO}_{1.95}(111)$ and the $\text{CeO}_{1.80}(111)$ films have roughly the same percentage of step defects, our observed higher heats of adsorption on the surface with a larger density of oxygen vacancies certainly support this conclusion.

No computational (e.g., DFT) work has been done to directly compare the binding strength of Au adatoms at oxygen vacancies to the binding at step sites. Castellani et al.¹¹¹ have attempted to investigate step defects by building a model that incorporates both concave and convex step morphology. For most model sites, these authors estimated by DFT that Au adatom adsorption energies were in the range of 0.52-0.69 eV at stoichiometric step sites, which was essentially the same as at stoichiometric terrace sites (0.51-0.66 eV). However, they did discover one step site that involves a concave facet intersecting the (111) plane and gave a Au adsorption energy that was three to four times higher (≈ 2.36 eV) than the above values.¹¹¹ Note, however, that these calculations gave an adsorption energy for Au at terraces that is much lower than those predicted by other DFT calculations (see below).

In comparison, DFT studies generally agree that oxygen vacancies on $\text{CeO}_2(111)$ terraces are more stable than stoichiometric sites for Au adatoms. When employing GGA + U calculations with $U_{\text{eff}} = 5$ eV Zhang et al. estimated that the adsorption energy of an Au adatom on an O-vacancy site on the terrace (2.75 eV) was roughly double that of the adsorption at the most stable site on the stoichiometric terrace (an O-O bridge) (1.17 eV).¹¹⁶ Similarly two-fold increases in the binding energy at oxygen vacancies compared to the most stable stoichiometric site were obtained by Hernandez et al.¹¹² (2.41 eV to 1.15 eV), and Camellone and Fabris¹⁴⁵ (2.29 eV to 1.18 eV). The largest difference comes from Chen et al.,¹⁰⁹ who calculated that Au binding at a surface oxygen vacancy (2.58 eV) was just slightly less than three times larger than at a stoichiometric O-top site (0.88 eV).

It is therefore evident from DFT that binding at oxygen vacancies is stronger than at stoichiometric terrace sites, certainly enough so as to affect the particle density. This is consistent with our observation of a two-fold larger particle density on $\text{CeO}_{1.80}(111)$ (with 10% of its oxygen atoms missing) compared to $\text{CeO}_{1.95}(111)$ (with 2.5% of its oxygen atoms missing). If our more reduced surface has the same 5% step density as our $\text{CeO}_{1.95}(111)$ surface, and if these are missing all of their oxygens, then the terraces on these more reduced films are missing only $\approx 6\%$ of their surface oxygen atoms. Additionally, vacancies have been observed to aggregate in reduced ceria films,¹⁴⁷ making the effective fraction of terrace defects likely smaller than 6%. Therefore, while our results do suggest that increased binding strength at surface oxygen vacancies on terraces increases the particle density, the experimentally and computationally observed strong binding of Au at steps – combined with the fact that binding is likely even stronger at more reduced steps (see above) – makes it difficult to unambiguously determine from the heat measurements whether steps with 50% vacancies bind Au more strongly than oxygen vacancy sites at terraces.

At 10 K, the dispersion of Au atoms and particles was found to be nearly random, indicating that low temperatures decrease the mobility of Au atoms.¹³⁵ Together with the observation of a higher particle density at 100 K, this supports the conclusion that the results presented here indicate an increased contribution from binding at stoichiometric terraces at 100 K versus 300 K, to explain the lower low-coverage heat on $\text{CeO}_{1.95}(111)$ at 100 K.

3.4.2 Au Particle Growth

Both the Au and the Ce signals in LEIS stop changing versus Au coverage above 1.6 ML on $\text{CeO}_{1.80}(111)$ at 300 K. This behavior was observed in three independent experiments on three separately prepared ceria films. The coverage at which this occurred was $1.6 \text{ ML} \pm 0.2 \text{ ML}$, with this variation likely the result of a small difference in the precise oxidation state for each ceria film

preparation. This signal saturation was *not* observed when Au was deposited on CeO_{1.80}(111) at 100 K, which suggests the presence of some type of thermal diffusion barrier.

The following explanation is proposed for this observation. What appears as a saturation of the LEIS signal is clearly due to a faster thickening of the Au particles (Fig 1(b)). If above some critical coverage or particle size, Au particles grow almost exclusively taller without growing laterally across the ceria surface, this would explain the relative LEIS signals. This would mean that incoming Au atoms prefer to nucleate a new Au layer on top of an existing Au particle rather than binding at its interface with the ceria. This seems counterintuitive, since binding to the edge of a large particle involves forming (on average) almost three Au-Au bonds to neighboring Au atoms in the bottom layer of the Au particle, plus additional bonds to the oxide surface below, while nucleating a dimer in a new layer would mean only 3.5 total Au-Au bonds per gold atom (with three of these to Au atoms in the Au layer below). This would require that the total bond strength to the oxide below for a new atom at the edge of the particle be weaker than $\approx 1/2$ of one Au-Au bond (i.e., $< 1/12$ the heat of sublimation, or < 31 kJ/mol). However, two effects could cause this. First, there may be particle-particle repulsions that cause their energy to increase dramatically as they grow larger in area and thus closer to each other. Second, and possibly related physically, the large lattice mismatch between Au(111) and CeO₂(111) likely produces lattice strain that increases with increasing particle diameter.¹⁴⁸ At some point, if the energy cost associated with this increasing strain gets too big, the Au may prefer to grow thicker rather than increasing the area of its interface with the ceria. This type of effect has been observed for Ag growth on Si(100).⁷⁸

3.4.3 Adhesion of Au Nanoparticles to CeO_{1.95}(111)

The value of adhesion energy of Au on CeO_{2-x}(111) measured here (2.53 J/m² for 3.6 nm diameter Au particles) is much higher than that for Au particles of 1-5 nm diameter onto MgO(100)

(0.67 J/m²), which was measured using contact-angle analysis in HRTEM.⁷⁶ Additionally, the adhesion energy of Au / CeO_{1.95}(111) is higher than for 3.6 nm diameter Ag nanoparticles on CeO_{1.90}(111) (2.3 J/m²),⁷⁰ but lower than for 2.2 nm diameter Cu particles on CeO_{1.95}(111) (3.52 J/m²).¹²⁶ It should be noted here that smaller particles typically have larger adhesion energies per unit area than large ones.⁵⁸ However, these values presented here for the adhesion energies of Au and Cu as determined by SCAC were obtained at the large-particle limit, before the probability of particle overlap became too high to apply the surface roughness factor for hemispherical caps.

This value can also compare these to the Au / Au adhesion energy, which is simply twice the Au surface energy. Using the value of 1.51 J/m² for the Au(111) surface energy,¹⁴⁹ the Au / Au adhesion energy (3.02 J/m²) is larger than the value that was measured for Au on CeO_{1.95}(111), but nearly equal to the adhesion of 2.6 nm Au particles on the reduced CeO_{1.80}(111) surface (2.93 J/m²). That the adhesion of Au / CeO_{1.95}(111) is less than Au / Au adhesion supports the observation that Au clusters into 3D particles rather than wetting the surface, and the similarity in the values between Au / Au adhesion and Au / CeO_{1.80}(111) can be explained by the strong contribution from local binding to defects.

Recently, Lin et al.¹⁰⁵ conducted a study with high-resolution aberration-corrected electron microscopy for 3-6 nm Au particles supported on ceria nanorods, which expose primarily the (111) face. Those samples were prepared using solution-based techniques and were post-annealed to 300 °C in air, so they may contain surface impurities, and thus cannot be directly related to our UHV-prepared Au / CeO_{2-x}(111) systems where surface cleanliness was verified spectroscopically. Nevertheless, they provide an interesting comparison. Based on the STEM-observed Au particle shape, they estimated that the adhesion energy of $\approx$ 5 nm Au particles to the (111) facets of ceria nanorods was 1.02 J/m².¹⁰⁵ This value was presented as the “interfacial free energy (γ_{int})”, and

was reported as negative value without a clear derivation of the specific equation used. However, a comparison to the Wulff-Kaichew theorem⁵⁸ revealed that this principle was the underlying relationship between particle shape and energy, but in this paper E_{adh} was replaced with $-\gamma_{\text{int}}$. Additionally, they used the same value for the Au(111) surface energy ($\gamma_{\text{v/m}} = 1.51 \text{ J/m}^2$,¹⁴⁹) that was used above in combination with our calorimetric heats. The value of E_{adh} measured here is 2.53 J/m^2 for 3.6 nm Au particles onto clean $\text{CeO}_{1.95}(111)$, which is 2.5 times their value. This discrepancy can be attributed to the role of surface impurities in their samples. Metal / oxide adhesion energies that are measured on clean surfaces in UHV have generally been found to be at least 2-fold larger than values measured on surfaces there were not verified to be clean.⁵⁶ This difference may also be related to the oxygen vacancies on our ceria surface, but the extent of reduction of their ceria samples is not quantitatively known.

3.5 CONCLUSION

Intensities in LEIS versus coverage showed that Au grows as 3D particles on slightly reduced $\text{CeO}_{2-x}(111)$ films at 300 K and 100 K. The Au particle density was nearly two times larger on the more reduced surface than on the more oxidized surface at 300 K, but only very slightly larger ($\approx 1.1\times$) at 100 K. The particle density at 100 K was also higher than at 300 K on both $\text{CeO}_{1.95}(111)$ and $\text{CeO}_{1.80}(111)$, due to slower adatom diffusion on the surface. While the LEIS intensities are consistent with the Au particles growing as hemispheres initially on both ceria surfaces at both 100 K and 300 K, once they exceed a certain size ($>2.5 \text{ nm}$ diameter), Au nanoparticles grown on $\text{CeO}_{1.80}(111)$ at 300 K were observed to thicken without spreading, achieving an aspect ratio (height to diameter) which was roughly twice as large as hemispherical caps. This was not observed at 100 K. Gold atoms adsorb 37 kJ/mol more strongly to the more oxygen-deficient $\text{CeO}_{1.80}(111)$ surface than to $\text{CeO}_{1.95}(111)$, similar to what was observed for Ag atoms, which

indicates stronger binding of both Au and Ag to oxygen vacancies than to the stoichiometric surface. The opposite was observed for Cu.¹²⁶ These differences between Ag and Au versus Cu arise from the greater oxophilicity of Cu, and are consistent with DFT calculations.^{109,116,143,145,150,151} At 100 K, the heat of Au atom adsorption at particle sizes <1.5 nm is lower than at 300 K, which is due to stronger binding of Au to steps (which are less accessible at 100 K due to slower Au diffusion). The heat of adsorption on all surfaces slowly increases with coverage to the bulk heat of Au sublimation by 2 ML. The adhesion energy of 3.6 nm Au particles on CeO_{1.95}(111) was found to be 2.53 J/m², and increased to 2.98 J/m² on CeO_{1.80}(111), albeit for smaller (2.6 nm diameter) particles.

3.6 FIGURES

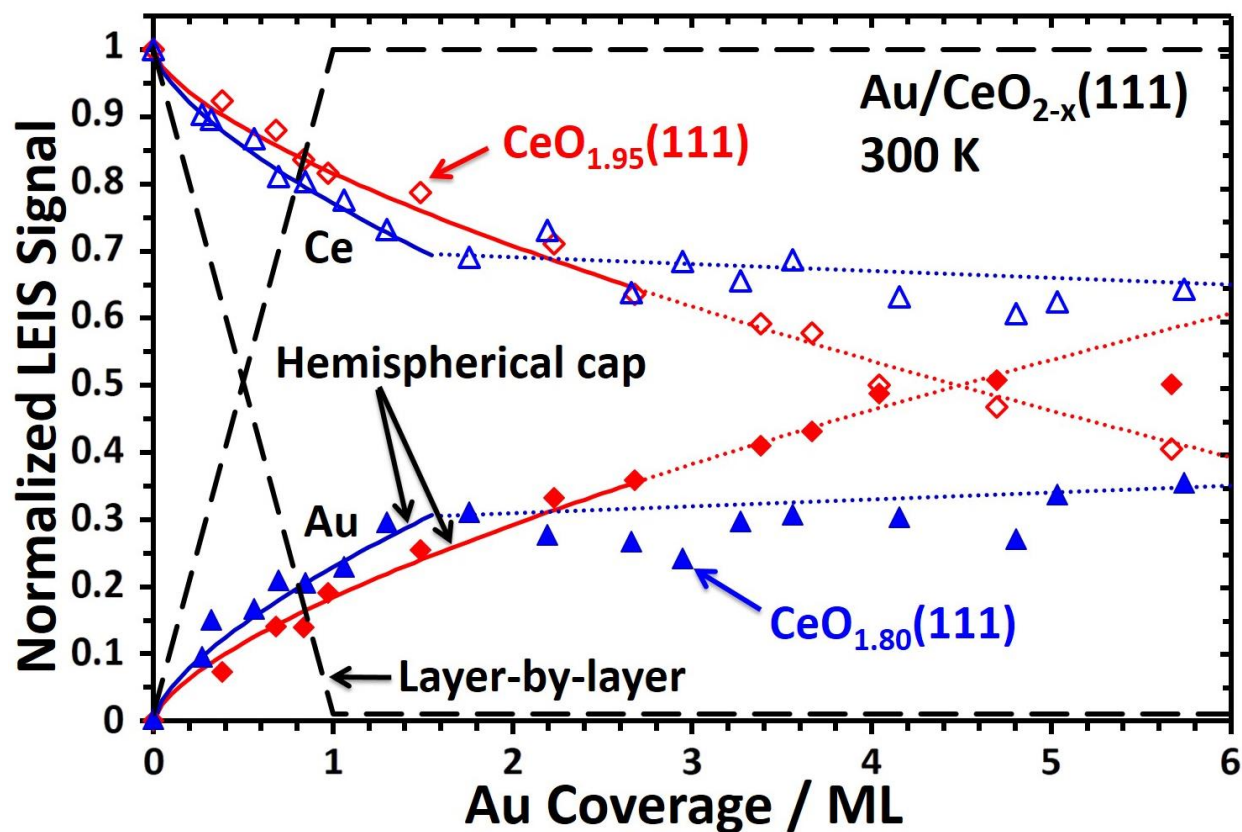


Figure 3.1. Integrated LEIS signal intensities for Au (closed symbols) and Ce (open symbols) as a function of total Au coverage on $\text{CeO}_{1.95}(111)$ (red diamonds) and $\text{CeO}_{1.80}(111)$ (blue triangles) at 300 K normalized to thick multilayer Au and clean $\text{CeO}_{2-x}(111)$ respectively. The dashed line corresponds to the normalized LEIS signal expected from a layer-by-layer growth mechanism while the solid lines correspond to Au growing as hemispherical caps with a fixed particle density of 2.8×10^{12} particles/cm² on $\text{CeO}_{1.95}(111)$ and 5.4×10^{12} particles/cm² on $\text{CeO}_{1.80}(111)$. This model only holds up the point where $\approx 35\%$ of the surface is covered by Au particles, since they could start to overlap at higher coverages. The dotted lines above the Au coverage which gives $\approx 35\%$ of the maximum LEIS signal change are shown to guide the eye.

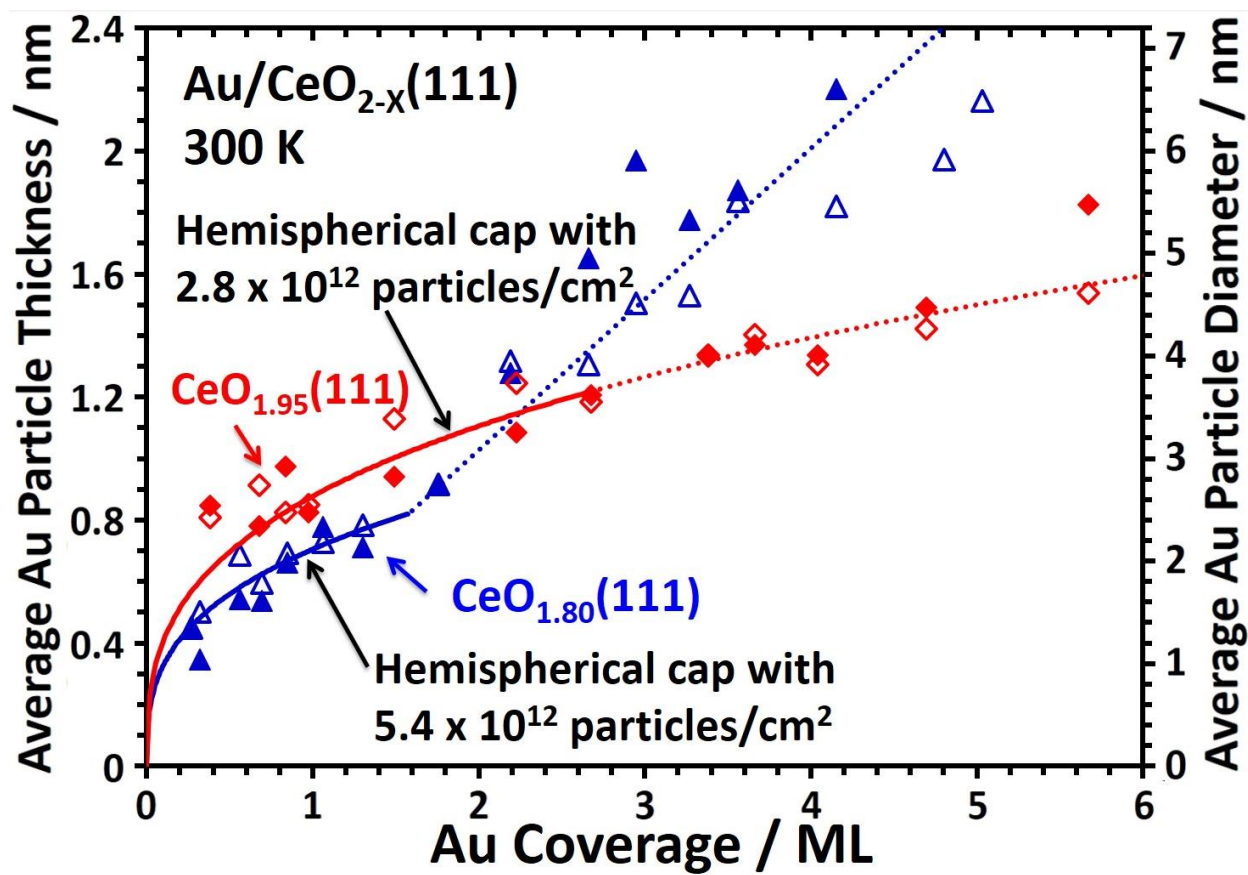


Figure 3.2. Average Au particle thickness as directly measured by LEIS (left axis) and the corresponding average Au particle diameter assuming hemispherical caps (= 3x thickness) (right axis) plotted versus Au coverage for both the more oxidized CeO_{1.95}(111) surface (red diamonds) and the more reduced CeO_{1.80}(111) surface (blue triangles) at 300 K. These thicknesses were measured using both the Au (closed) and the Ce (open) LEIS data shown in Figure 3.1. The solid curves shown are the expected result from the same hemispherical-cap model and particle number densities as used for the best fit to the data in part (a). The dotted curves are only to guide the eye. The average particle thickness on the reduced surface starts to grow much faster than this hemispherical-cap model above 1.6 ML, suggesting that these particles are growing with an aspect ratio that is thicker than hemispherical caps.

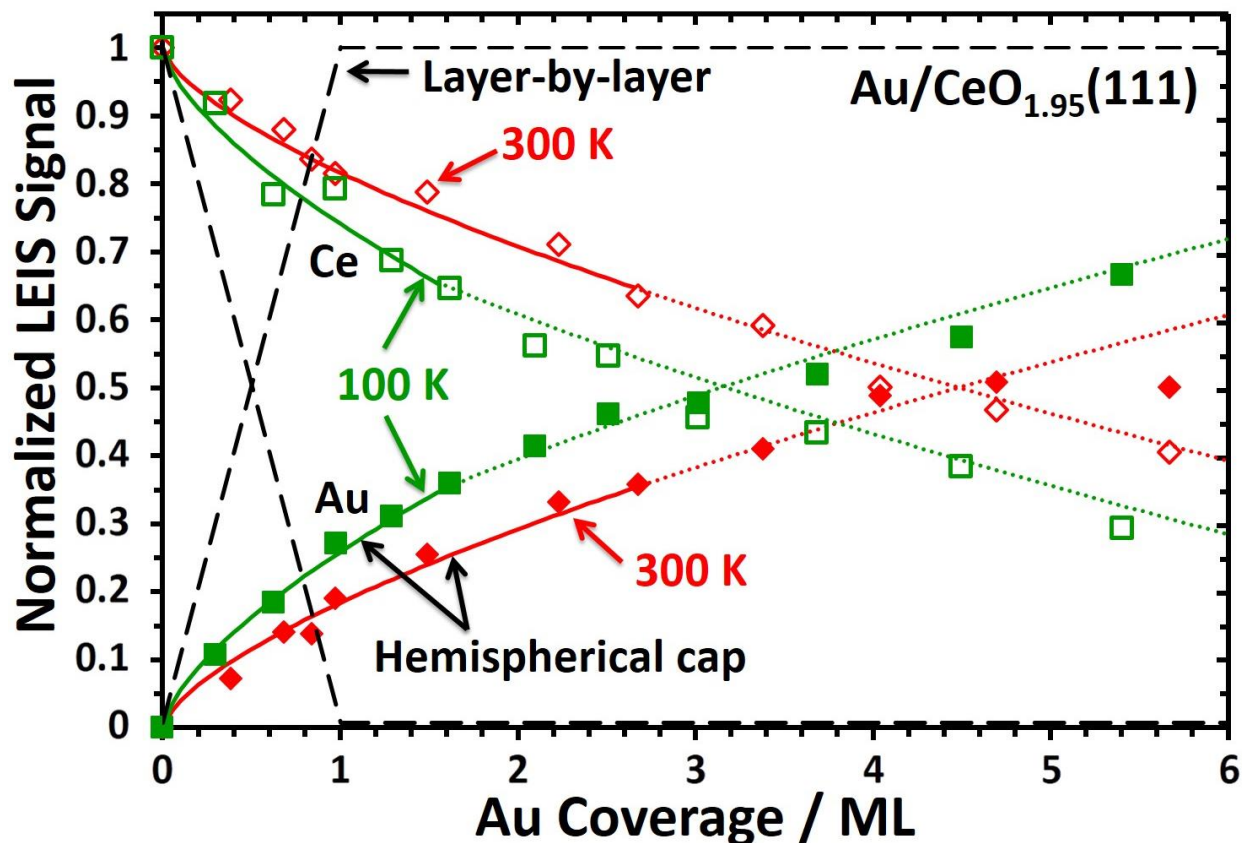


Figure 3.3. Integrated LEIS signal intensities for Au (closed symbols) and Ce (open symbols) as a function of total Au deposited onto CeO_{1.95}(111) at 300 K (red diamonds) and at 100 K (green squares) normalized to the signal for thick multilayer Au and clean CeO_{2-x}(111), respectively. The dashed lines correspond to the signals expected from a layer-by-layer growth mechanism while the solid lines correspond to Au growing as hemispherical caps with a coverage-independent particle density of 2.8×10^{12} particles/cm² at 300 K and 7.8×10^{12} particles/cm² at 100 K, and a single-particle diameter at any one coverage. The dotted lines above the Au coverage which gives $\approx 35\%$ of the maximum LEIS signal change are shown to guide the eye.

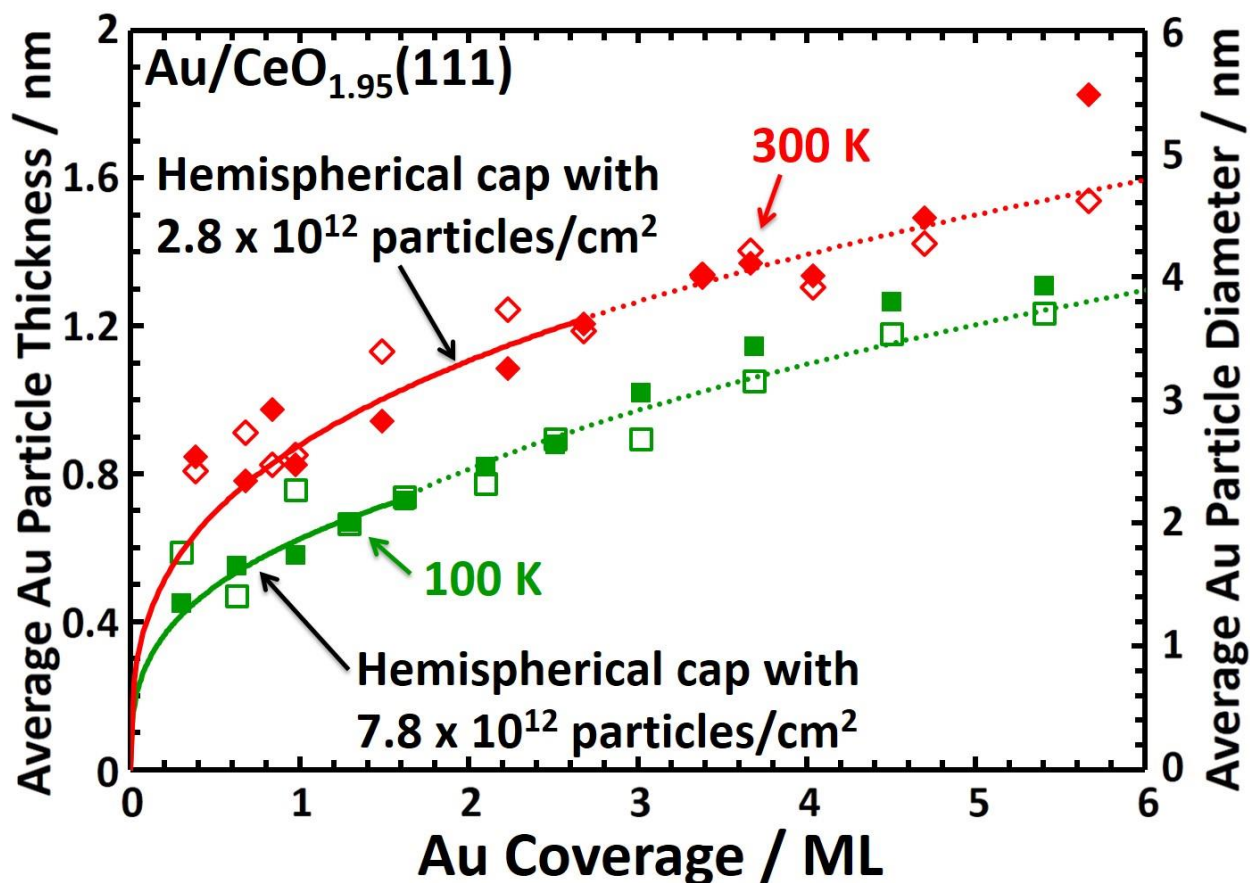


Figure 3.4. Average Au particle thickness that comes directly from LEIS data (left axis) and the corresponding average Au particle diameter ($= 3 \times$ thickness) assuming hemispherical caps that (right axis) plotted versus Au coverage on CeO_{1.95}(111) at 300 K (red diamonds) and 100 K (green squares). Thicknesses were measured using both the Au (closed) and the Ce (open) LEIS data of Figure 3.3. The solid curves shown are the expected result from the same hemispherical-cap model and particle number densities as used for the best fits to the data in part (a). Dotted curves above that are to guide the eye.

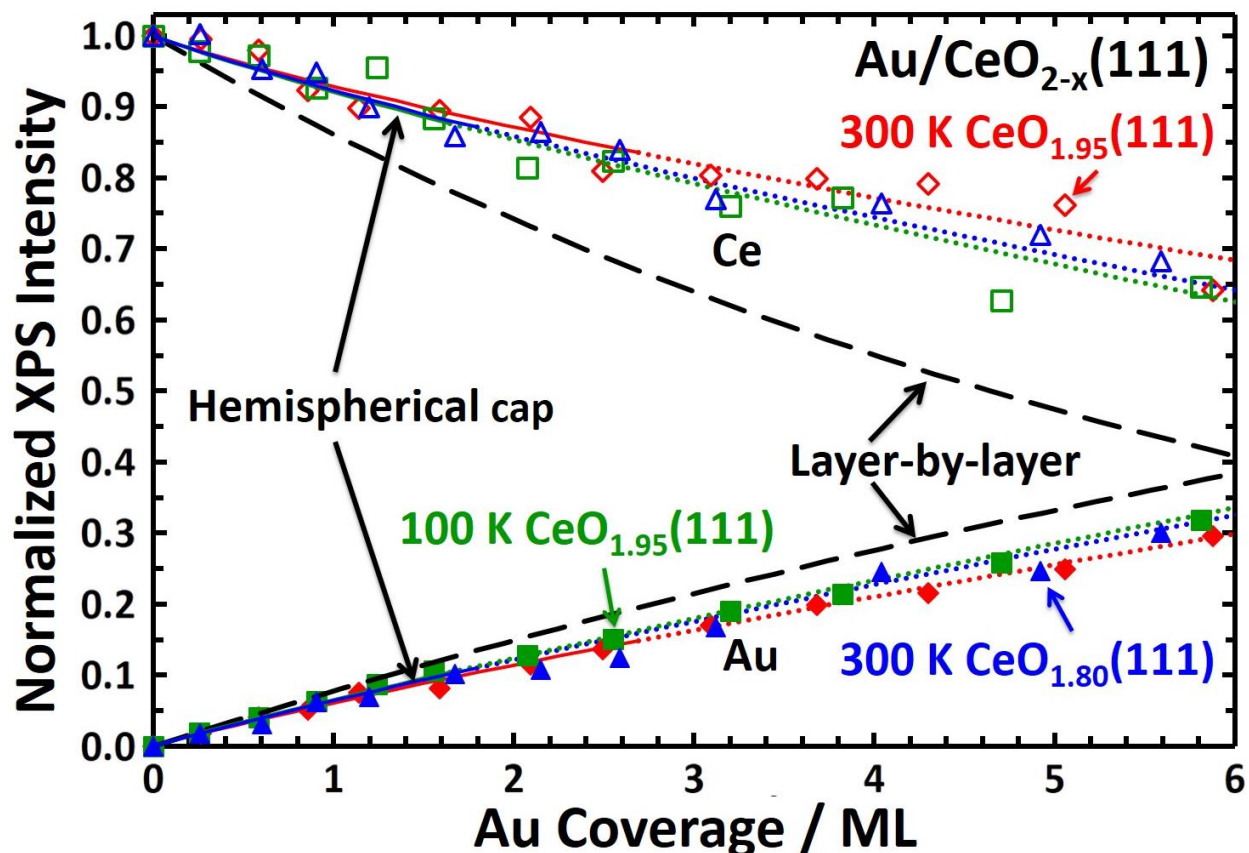


Figure 3.5. Integrated Au 4f_{5/2} (closed) and Ce 3d (open) XPS signal intensities (detected normal to the surface) normalized to thick Au (>60 ML) and clean CeO_{2-x}(111), respectively, versus Au coverage. These data for Au deposition onto CeO_{1.95}(111) at 300 K (red diamonds), CeO_{1.80}(111) at 300 K (blue triangles) and CeO_{1.95}(111) at 100 K (green squares), are well fitted by the dotted lines, which correspond to Au growing as hemispherical caps with a fixed particle density of 2.8×10^{12} particles/cm², 5.4×10^{12} particles/cm², and 7.8×10^{12} particles/cm², respectively. (This model is only intended to be valid up to 1.6-2.6 ML, see Figure 3.3). The good agreement further supports the hemispherical-cap models. The layer-by-layer growth model (dashed lines) does not fit the data above 1-2 ML.

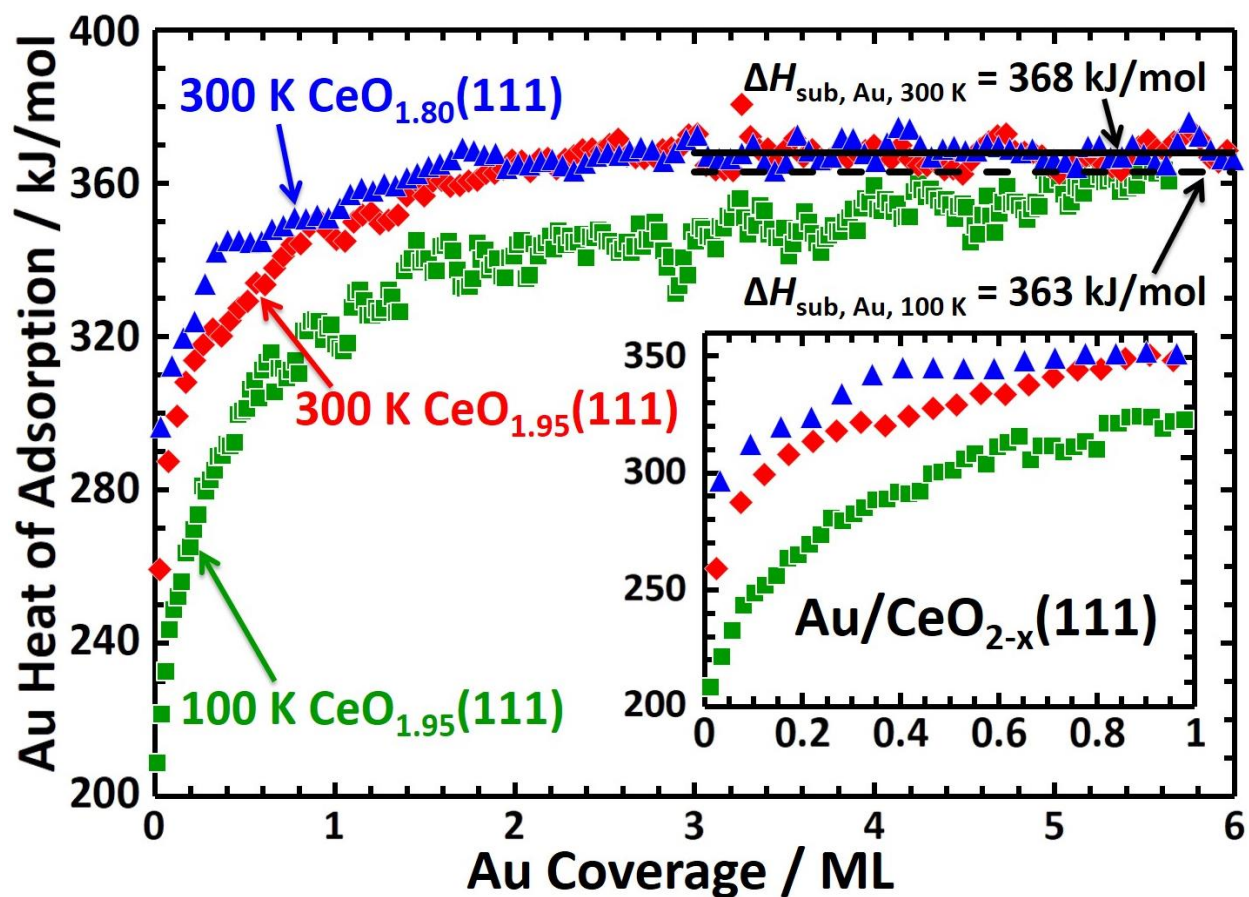


Figure 3.6. Heats of Au atom adsorption on CeO_{1.95}(111) at 300 K (red diamonds) [average of 5 experiments], CeO_{1.80}(111) at 300 K (blue triangles) [average of 3 experiments] and CeO_{1.95}(111) at 100 K (green squares) [average of 3 experiments] as a function of total Au coverage (1 ML = 7.89×10^{14} atoms/cm²). The inset expands the range from 0-1 ML where the heat changes most rapidly with coverage.

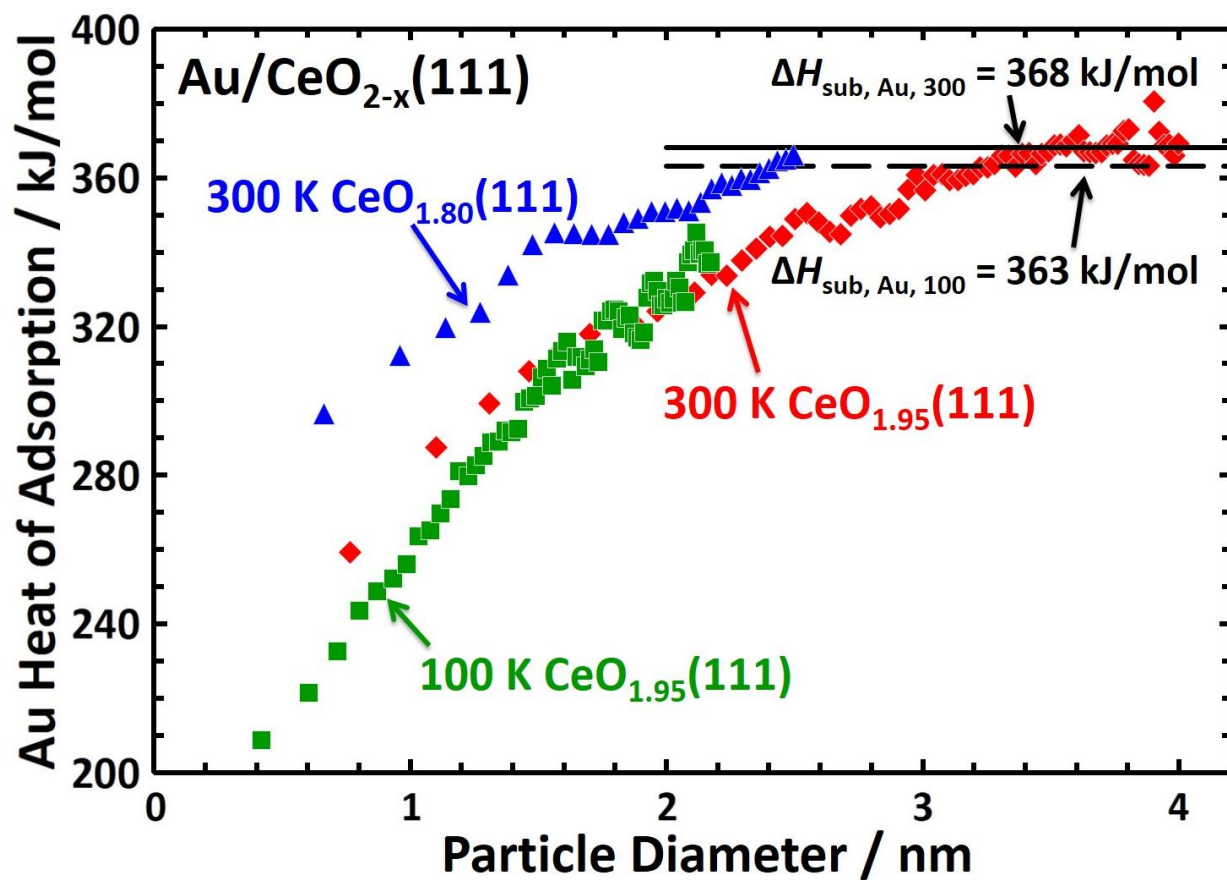


Figure 3.7. Heats of Au atom adsorption on CeO_{1.95}(111) at 300 K (red diamonds), CeO_{1.80}(111) at 300 K (blue triangles), and CeO_{1.95}(111) at 100 K (green squares) from Figure 3.6, plotted as a function of the average Au particle diameter to which Au atoms add.

Chapter 4. Energetics of Au 2D Islands and 3D Nanoparticles on MgO(100): Influence of Defects on Adsorption and Adhesion Energies

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The adsorption of Au vapor onto MgO(100) films grown on Mo(100) was studied at 300 and 100 K using single-crystal adsorption calorimetry (SCAC). The Au morphology was investigated using He⁺ low-energy ion scattering spectroscopy (LEIS) and X-ray photoelectron spectroscopy (XPS). A detailed shape analysis from STM literature¹⁵² combined with the LEIS data reveals that Au grows as 2D islands with bilayer thickness (≈ 0.41 nm) within the first 0.4 ML of Au coverage at both 300 and 100 K. The island density is 3.0×10^{11} particles/cm² at 300 K and 5.4×10^{11} particles/cm² at 100 K. These 2D bilayer Au islands grow to a diameter of ≈ 7 nm, at which point they thicken, becoming taller significantly faster than they increase in diameter. The initial sticking probability of Au on MgO(100) is 90% at 300 K and 95% at 100 K, and increases with coverage. The maximum surface residence time of the Au atoms that do not stick is <10 ms, implying that gold monomers bind to MgO(100) weakly (<68 kJ/mol at 300 K, and <22 kJ/mol at 100 K). The adsorption energies indicate that Au particles of the same size bind more strongly to MgO(100) when grown at 300 K than at 100 K, which can be attributed to Au binding to step edges (or other topological defects) at 300 K, but at perfect MgO(100) terraces at 100 K (because Au diffusion is too slow to find defects). The adsorption energy of Au onto 31-atom Au clusters is 285 kJ/mol at 300 K, ≈ 68 kJ/mol higher than at 100 K. This result is attributed to the difference between particles on defects versus terraces. Similarly, the adhesion energy of Au nanoparticles to MgO(100) extracted from the adsorption energies at 300 K is much higher (1.81 J/m² for ≈ 7 nm

particles at defects) than at 100 K (0.31 J/m^2 for $\approx 7 \text{ nm}$ particles at terraces). This value at 100 K is close to the adhesion energy estimated from electron-microscopy shape measurements of Au particles at terraces on MgO(100) ($0.45\text{-}0.67 \text{ J/m}^2$). The heat of Au adsorption increases from 210 to 340 kJ/mol as the 2D island size increases from 0.7 to 7 nm diameter, and then to the bulk sublimation enthalpy ($\approx 368 \text{ kJ/mol}$) as they thicken to 2 nm. This is the first experimental measurement of any metal adsorption energy as a function of island diameter when forming 2D islands, as well as the first direct comparison of any adhesion energy found from calorimetric adsorption energies to that from particle shape analysis.

4.1 INTRODUCTION

Supported gold nanoparticles have attracted significant attention in the last decade as potential catalysts for CO oxidation, selective oxidations, and other industrially-relevant reactions, as well as in the fields of photonics, plasmonics, nanotechnology, and biology.^{16,25,153} Despite the fact that gold is inert in its bulk form, recent progress in nanotechnology has revealed that gold nanoparticles between 1 and 6 nm are catalytically active for a variety of different reactions.^{12–15} Most notably, gold nanoclusters dispersed across high-surface-area metal oxide supports have shown great potential as low-temperature CO oxidation catalysts,^{14,19,24,154,155} which is surprising given that both gold and the oxide support are often inactive for CO oxidation on their own. The catalytic properties of such oxide-supported gold nanoparticles depend strongly on both the size of the nanoparticles and the properties of the oxide (surface structure and orientation, reducible or non-reducible, defect concentration, etc.). Significant strides towards understanding the origin of these effects have been made within the last several decades by studying well-defined model systems in ultrahigh vacuum conditions,^{53–55} with Au nanoparticles on MgO(100) being one of the most intensively studied model catalysts.^{28,29,76,137,152,156–167} Here, calorimetric measurements of

the adsorption energies of Au atoms as they nucleate and grow nanoparticles on MgO(100) are reported by using temperature to control the location of those nanoparticles at terrace and defect sites, and extract from these the Au / MgO(100) adhesion energies and particle size dependence of the Au atom chemical potential. Surface-sensitive spectroscopy is also used to study Au growth morphology, which is then used to report for the first time the chemical potential of Au atoms in Au nanoparticles on MgO(100) as a function of particle size. Also reported here are the first ever measurements of the heat of adsorption of any metal atom in making 2D islands and their chemical potential as a function of 2D island diameter (from 0.7 to 7 nm) and the number of atoms per island (from 10 to 2000). The effects of defect sites on these energies are also explored in this chapter.

Among the oxide surfaces studied in model catalysts, MgO(100) is one of the most prevalent. MgO is a simple stoichiometric binary oxide with a rocksalt structure and well-defined surfaces that are stable under most operating conditions. The most stable (001) surface has only minor structural differences from the bulk,¹⁶⁸ has very poor electron transfer properties, and can be prepared readily by cleavage,^{169,170} by the production of MgO smoke,^{76,171} or by thin-film growth.^{60,172–176} However, despite several decades of attention, much remains unclear about this insulating oxide surface. Specifically, it has been observed that defects are critical contributors to the physical and chemical properties of MgO, and play a dominant role in the adsorption behavior of its surfaces (an excellent review of the complexity and significance of these defects is presented in ref ¹⁶⁸). For example, while bulk MgO does not absorb or emit light between 200 and 900 nm, luminescence bands have been observed in MgO smoke^{171,177,178}, MgO powders^{179,180} and in defect-poor MgO(100) films¹⁸¹ at energies that are significantly lower than the bandgap, which Benedetti et al.¹⁸¹ assigned to under-coordinated corner sites (3-fold) and step edges (4-fold). Whereas a defect free MgO(100) surface does not interact with CO^{182,183} or CO₂,¹⁸⁴ MgO powders

are highly reactive to CO.¹⁸⁵ The nature and the identification of these defects, as well as their effects on adsorption and catalytic properties, is still under debate.

For several decades, the primary defect of interest was the surface oxygen vacancy or F-center, which can contain localized electrons^{186,187} and can be produced on MgO(100) by electron bombardment.¹⁸¹ Au is known to nucleate preferentially on F-centers in MgO(100),^{160,163,188,189} and it has been predicted by theory^{16,189–193} and confirmed by experiment¹⁶⁴ that F-centers can transfer electronic charge to supported metal nanoparticles. UHV experiments showed that 8-atom Au clusters deposited on defect-free MgO(100) supports were essentially inert, whereas Au clusters of this same size were active towards CO on highly defective MgO(100) films.^{16,193} Furthermore, shifts in CO FTIR spectra¹⁹⁴ indicate that small Au clusters bound to electron-rich defects form negatively charged species. For decades, this evidence pointed to oxygen vacancies as the primary activators of supported metal nanoparticles, which contributed to the belief that F-centers are present in relatively high concentrations on the surface of as-prepared MgO(100) samples. However, recent results show that the number of F-centers on MgO surfaces is very low unless MgO is specifically treated to create them, and vacancy defects alone cannot explain many of the observed features in MgO reactivity.¹⁶⁸

Possible candidates to replace the F-center model are four-coordinated Mg and O ions located at steps or edges, or the defects formed by the intersection of two MgO steps perpendicular to each other, known as a reverse corner.^{195,196} Au particles have been shown to preferentially nucleate at step edges over terraces on MgO(100) at 300 K and above,^{137,165,169,170,197,198} and experimental evidence suggests that these morphological defects in MgO(100) films can also act as strong electron traps.^{168,196} Additionally, hydroxyl groups on the oxide surface may act as sites for bound electrons, and hydroxylated MgO(100) surfaces have been shown to oxidize Au

particles¹⁹⁹ and enhance the stability of Au clusters against thermal sintering.²⁰⁰ Whereas UHV conditions minimize the concentration of such impurities on the surface, even a trace concentration of water may decorate the oxide steps with OH groups.

When MgO(100) films are grown on Mo(100), as done here, STM shows that the mismatch between Mo and MgO causes a Moire pattern to form when films are less than ≈ 5 ML thick.¹⁸¹ Above this thickness, the dominant defects are step edges and screw dislocations that align into a dislocation network. These electron-rich dislocation defects persist until thicknesses of over 10 ML, however STM imaging above 15 ML is difficult due to decreasing conductivity of the films.¹⁸¹ It is impossible to prepare a completely defect-free oxide film, and it is reasonable to assume that the most common type of defects present in our films are step edges and corners. The MgO(100) films prepared in this investigation are thick enough (≈ 3.5 nm) that dislocation lines are likely scarce, but they may still be present in small quantities. Additionally, the preparation conditions ensure a negligible concentration of F-centers and surface hydroxyls, which is confirmed by the absence of spectroscopic signal due to such species, therefore their presence does not explain the adsorption behavior of Au. We propose that because Au has such a high electronegativity, it is likely that even a small concentration of morphological defects (i.e. steps, corners) affects the measured calorimetric binding strength of Au, as well as the morphology of Au particles that are vapor-deposited onto MgO(100) films. For this reason, the experiments presented here are conducted on highly-ordered, ≈ 3.5 nm thick, defect-poor MgO(100) films at both 300 K and 100 K. At lower temperatures, Au atoms diffuse more slowly, which increases the probability that Au particles will nucleate at less favorable terrace MgO(100) sites rather than steps or edges. Conducting these experiments at a lower temperature allows for a direct experimental comparison

of the adsorption and adhesion energies, as well as the morphology, of Au particles adsorbed at terraces versus defect sites.

4.2 EXPERIMENTAL DETAILS

A detailed description of the adsorption microcalorimetry apparatus and experimental procedure is presented in Chapter 2. The MgO(100) films were grown in an adjacent UHV preparation chamber on the front-face of a 1 μm thick single-crystal Mo(100) sample, which is ≈ 8 mm in diameter, as described below. Au coverage is given throughout in ML, where 1 ML is equal to the surface atomic density of MgO(100) (1.12×10^{15} atoms/cm²). The Au was purchased from Kurt J. Lesker with 99.99% purity.

The Mo(100) surface was cleaned by thermal annealing to 1600 °C in UHV for 1-2 minutes until no C was present in XPS and a sharp Mo(100) LEED pattern was observed. Because the Mo(100) films were very thin, excessive heating risked damage to the crystals (creating small holes and tears). Therefore very small quantities of O were sometimes still observable on the Mo(100) by XPS after this annealing treatment. This small amount of O did not measurably affect either the Mo(100) or the MgO(100) LEED quality, the XPS spectra of the grown MgO(100) films, or the calorimetric results. The MgO(100) films were grown via reactive evaporation of Mg (Kurt J. Lesker, 99.95%), first in UHV at 25 °C for 1 minute, and then in a 1×10^{-6} Torr O₂ background gas at a sample temperature of 300 °C. The as-grown films were then annealed at 550 °C in this same background pressure of oxygen for 2 minutes to ensure a minimal concentration of oxygen vacancies.

4.3 RESULTS

4.3.1 MgO(100) Thin Film Characterization.

Thin films of MgO(100) were grown in a connected UHV chamber to a thickness of 3.5 ± 0.7 nm (≈ 13 -20 MgO(100) layers) on a 1 μ m thick Mo(100) substrate as described above. This thickness was obtained by depositing Mg onto Mo(100) at 300 °C in 1×10^{-6} Torr O₂ for four minutes while maintaining a constant QMS signal for Mg ($m/e = 24$), and then measuring the attenuation of the Mo 3p_{3/2} peak with XPS to give the MgO(100) film thickness, and thus the deposition rate. The average MgO deposition rate was 0.1 nm/min as determined by the attenuation of the Mo 3p_{3/2} photoelectron peak, using the inelastic mean free path of Mo 3p_{3/2} electrons escaping through MgO calculated using NIST inelastic mean free path database (25.7 Å). Once this rate was determined, MgO(100) films were grown at the same conditions while maintaining this constant QMS signal magnitude (i.e., Mg flux) for the amount of time needed for the desired 3.5 nm thickness. The (100) surface order was verified by LEED, which gave a sharp (1 x 1) square pattern. The one-to-one ratio of Mg to O was confirmed by comparing the relative magnitudes of the Mg 2s and O 1s signals, corrected for atomic sensitivity factor and instrument response function. No carbon, other elements, nor metallic Mg were observed in XPS. All the films were annealed at 700 °C in O₂ for two minutes after initial growth, however this annealing did not affect the quality of the LEED or the XPS spectrum.

MgO(100) films grow epitaxially with their (001) planes parallel to Mo(001) and the MgO(100) direction aligned with Mo(110), which is due to the 5% lattice mismatch between body-centered cubic Mo ($a = 3.15$ Å) and rocksalt MgO ($a = 2.98$ Å).¹⁸¹ It has been shown previously for the case of CeO₂(111) that oxide film thicknesses greater than 2 nm produce bulk-like adsorption properties.⁷⁰ However, in the case of MgO(100) films, it has been observed that larger

thicknesses (>15 layers, i.e., >3.1 nm) are required to produce flat, defect-poor films.^{181,201} When our films were thinner than 13 layers (≈ 2.7 nm), the observed LEED spots were substantially more diffuse than the ≈ 3.5 nm-thick films used below.

4.3.2 Au Sticking Probability on MgO(100) at 300 K and 100 K.

The sticking probability of Au atoms onto MgO(100) as a function of total Au coverage was measured by monitoring the number of non-sticking Au atoms in each pulse. This sticking probability was determined as previously described⁷² by comparing the magnitude of the time-integrated transient QMS signal for Au vapor during each calorimetry pulse to a zero-sticking reference signal that was generated by placing a hot Ta foil flag in the sample position and resistively heating it so all of the incoming Au atoms rapidly desorb. The fraction of atoms that did not stick was then used to scale the absorbed heat per pulse in kJ/mol and the cumulative total Au coverage. The sticking probabilities versus coverage for both 300 K and 100 K are shown in Figure 4.1.

At 300 K, the sticking probability starts high at 90%, as expected for metals with large bulk cohesive energies, and then increases to unit sticking probability, which it approaches (to within 1%) at ≈ 2 ML. At 100 K, the sticking probability starts higher, at 95%, and reaches unity more rapidly (by ≈ 1.5 ML). Measured sticking probabilities that are above 90% is consistent with what the Campbell group found for other late transition metals (Cu and Ag) on MgO(100).⁶⁴

4.3.3 Au Particle and Film Morphology on MgO(100) Observed with LEIS and XPS.

The Au nanoparticle morphology on MgO(100) at 300 K and 100 K was tracked with He⁺ LEIS as shown in Figure 4.2. Discreet quantities of Au were deposited using similar dose rates as those used during calorimetry. The attenuation of the Mg and O LEIS substrate signals and the

growth of the Au adsorbate signal were monitored as a function of total Au coverage. The integrated Mg and O LEIS peak areas were normalized to the signals from the clean MgO(100) film prior to Au deposition. The integrated Au peak areas are typically normalized to a high-coverage point where no substrate signal is visible, however even at very high Au coverages (>50 ML), the Mg and O LEIS peaks were still visible, and this was repeatable across multiple runs. The integrated areas of these substrate peaks were typically $\approx 15\text{-}30\%$ of the initial clean Mg and O signals at both 300 K and 100 K (though routinely less at 100 K), and the two values were always within $\approx 2\%$ of each other. Therefore, to represent the signal for a bulk-like continuous Au overlayer, the final highest-coverage integrated Au peak area was scaled by $(1 - S/S_0)$, where S/S_0 is the average of the remaining Mg and O signals relative to their initial values. This scaled Au signal was used to normalize the Au LEIS peaks.

To ensure that no significant ion damage was done to the sample by He^+ ion bombardment during the LEIS experiments in Figure 4.2, control experiments were conducted in each case using only four coverage points: 0 ML, 0.6 ML, 3 ML, and >60 ML. The zero and “full” coverage points are used for normalization, and the two intermediate points were chosen at signals that are still highly sensitive to small changes in coverage. This procedure resulted in four-fold less total ion beam exposure at those points, and the data from these experiments fell within error of the data in Figure 4.2. This indicates that He^+ ion beam damage did not significantly affect the LEIS results.

From 0-0.4 ML, the integrated Au LEIS signals increase nearly linearly with a slope of approximately 1/2 at both 300 K and 100 K. Above this coverage, the Au signal increases much more gradually with coverage. This behavior of the Au LEIS signals is mirrored by the Mg and O signals at both temperatures, which decrease with the same trend. The normalized Au LEIS peaks

at 100 K are always slightly larger than the normalized signal at 300 K, and similarly the Mg and O normalized LEIS signals at 100 K are always slightly smaller than those at 300 K.

Since LEIS is sensitive only to the topmost atomic layer, the normalized overlayer and substrate signals represent a nearly direct measurement of the fraction of the oxide surface that is masked and unmasked, respectively, by adsorbed nanoparticles.¹²⁹ From this, it is clear that only $\approx 35\text{-}40\%$ of the surface is covered by Au at 6 ML.

If Au was growing on MgO(100) in a layer-by-layer fashion, the normalized Au LEIS signal would increase linearly with a slope of one (reaching 100% of the surface covered by 1 ML). There is an observable linear change in signal from 0-0.4 ML, but the slope of one half suggests that Au is growing as 2D islands with bilayer thickness in this region. The “roll over” that occurs at ≈ 0.4 ML suggests that the morphology of Au films above this coverage is different from this bilayer-island morphology, in that the thickness is quickly increasing, as in 3D nanoparticles.

When 2D or 3D metal particles grow during vapor deposition on oxide surfaces, it is generally observed that after a nucleation stage (which only requires a few percent of a monolayer to complete), the number density of particles reaches a saturation value, and thereafter does not change substantially until the particles start to become so big that they overlap and fuse.^{42,134,138} Indeed, even while the particle *shape* is changing, it has been observed with TEM^{197,202} and AFM¹⁶⁵ that when Au is vapor-deposited onto bulk-like MgO(100) crystals that the particle *density* first rapidly increases (nucleation) and then remains constant (growth) over a large coverage range until the Au particles become large enough to coalesce. This result has similarly been observed with STM for Au that is deposited onto thin films of MgO(100) grown on Mo(100), where the particle density similarly remains nearly constant (within a factor of two) until the coalescence regime is reached.¹⁶³ It is therefore reasonable to assume constant number density of Au particles

in analyzing the LEIS data here from the lowest Au coverage studied up to a coverage where $\approx 35\%$ of the surface is covered by Au.

The morphology of 3D metal nanoparticles grown on oxide surfaces is often modeled with the hemispherical-cap model, which assumes that the nanoparticles grow with a hemispherical shape and constant particle density, changing in size only.^{130,131} Since the normalized LEIS signals directly measure the fractional coverage, the normalized Au signal can be modeled as:

$$I/I_0 = f_s = n(A_{\text{particle,int}} + A_{\text{shadowed}}) \quad (4.1)$$

where n is the particle density in particles/cm², $A_{\text{particle,int}}$ is the interfacial area per particle, and A_{shadowed} is the additional footprint area of the substrate that is shadowed from the incident ion beam or detector by the particle.¹³¹ This equation is valid when the particles all have the same size and shape. For the shape of hemispherical caps in our LEIS analysis geometry, where the incident ion beam is parallel to the surface normal and the angle of detection is 45 degrees from the surface normal, this equation becomes:

$$f_s = 1.207n\pi R^2 \quad (4.2)$$

where R is the hemispherical particle radius.¹³¹

However, as shown below, these LEIS data are not fit well by the hemispherical-cap model at all coverages with any single particle density. Therefore, in order to model the LEIS data, we turn to published STM data for evidence of the particle shape. Benedetti et al.¹⁵² observed that Au particles grown on 2-2.5 nm thick MgO(100) films at 300 K had flat-topped triangular and hexagonal shapes in the region from 0-5 ML Au coverage, typically oriented with one of their three or six edges aligned with a MgO(110) direction. These Au particles has the lowest aspect ratio of all metals studied on MgO(100),¹⁵² defined as the ratio of particle's maximum height to the longest interfacial axis. This aspect ratio is not constant over the entire coverage range studied

by STM, which explains the failure of the hemispherical-cap model here, as it requires that the particle shape remain constant.

Next the Au particle density is determined based on the LEIS data at a single coverage where the geometry of the system is known (by using the STM observations of a similar system, such as those measured by Benedetti et al.¹⁵² described above). By assuming that this particle density remains constant with coverage, the LEIS data at other coverages is then interpreted in terms of both particle shape and size.

At 2 ML Au coverage on MgO(100) at 300 K, Benedetti et al.¹⁵² observed with STM that the flat-topped Au nanoparticles have different orientations and an average aspect ratio of 0.3. It is reasonable to make the simplification that an array of flat-topped triangular and hexagonal shapes with different orientations can be roughly described as averaging out to a collection of flat circular disks, so that the shadowed area does not depend on particle's orientation. With a 45-degree detection angle, the shadowed area is the diameter of the disk multiplied by its thickness, which is directly related to the aspect ratio. For the observed aspect ratio a of 0.3 at 2 ML, we obtain:

$$I/I_0 = f_s = n(\pi R^2 + 1.2R^2) = n\pi R^2(1 + 1.2\pi) = 1.382n\pi R^2 \quad (4.3)$$

This equation for modeling the LEIS data is functionally identical to that for hemispheres above, with a slightly larger prefactor of 1.382 instead of 1.207 due to more macroscopic shadowing. The value of R at any given coverage can be determined by the total amount of Au deposited d expressed as the average Au thickness (i.e., d = the Au coverage in atoms per unit area times the volume per atom in bulk Au(solid)), given by:

$$d = nV_{\text{particle}} = n\pi R^2(t) = n\pi R^2(2aR) = 2na\pi R^3 \quad (4.4)$$

where V_{particle} is the volume per disk-shaped particle. At ≈ 2 ML where $a = 0.3$ and $d = 0.38$ nm this gives $R = 1.26n^{-1/3}$. Substituting these values into Equation 4.3 above and using $I/I_0 = 0.215$ from the LEIS measurement at 2 ML at 300 K gives a particle density of $n = 3.0 \times 10^{11}$ particles/cm². (Here the Au, Mg, and O normalized LEIS data are combined to best estimate I/I_0 .) Assuming that the same particle shape at 2 ML and 100 K as observed by STM at 2 ML and 300 K (above) gives a number density of 5.2×10^{11} particles/cm² at 100 K. The higher density at 100 K is consistent with the general trend that particle densities are higher at lower temperatures.^{42,68,127,138,203} By comparison, if instead hemispherical shapes were assumed at this same coverage, the particle density that best fits the 2 ML data is 5.5×10^{11} particles/cm² at 300 K, and 1.0×10^{12} particles/cm² at 100 K. It should be noted that these n values are slightly larger due to the effects of assumed shape on both the shadowing factor and the relationship of R to the volume per particle.

The LEIS data can be replotted to show the average Au particle thickness as a function of total Au deposited. By dividing this average film thickness d at each coverage by the fractional area covered by Au particles as measured by LEIS (using the Au, Mg, or O normalized signal, modified by the macroscopic shadowing factor), the average Au particle thickness is obtained, similar to previous reports.^{126,203} Although this transformation requires an assumption of a macroscopic shadowing factor which depends on particle shape, which has been established to likely be changing, this dependence is weak enough that a reasonable approximation can be made by assuming that it is constant at the value for an aspect ratio of 0.3 (i.e., 1.382, see above). Figure 4.3 shows the data in Figure 4.2 replotted in this way as the average Au particle thickness versus coverage at both 300 K and 100 K. Additionally, the lines indicate the thickness that would be

expected from the disk-model with a fixed aspect ratio of 0.3 assuming the same particle density found in Figure 4.2.

As seen in Figure 4.3, at low coverage the Au particles are thicker than single-layers (indicated by the dashed line), but significantly thinner than the fixed-aspect-ratio model predicts. On the other end above 2 ML, the particles are much thicker than the model suggests. In other words, their aspect ratio is initially lower than 0.3, and then increases well above this value, suggesting that the particles are growing thicker far faster than they are growing laterally across the surface. These data are reanalyzed below without any assumption about the macroscopic shadowing factor, and similar results are obtained, with these conclusions even more obvious.

Since the particle densities remain constant with coverage at both 300 K and 100 K (at the values found above at 2 ML), and the Au particles have flat tops according to STM (see above), it is assumed here that they remain approximately disk-shaped, and estimate their aspect ratio a and effective radius R at every coverage. These parameters are related through the total thickness of Au film, d , given by Equation 4.4 and the fractional area masked in LEIS by the gold particles, f_s , given by the number density of particles times the surface area of the top-face of the disk plus the extra area of the substrate that is shadowed from the detector by the disk at the detection angle of 45° from normal:

$$f_s = n(\pi R^2 + 4aR^2) \quad (4.5)$$

These two relationships provide a system of two equations with two unknowns, a and R , for each coverage. The diameters and aspect ratios that result from this analysis are shown in Figure 4.4(a) and Figure 4.4(b).

As seen at both 300 K and 100 K, the aspect ratio of the particles increases as the total Au deposition increases, reaching approximately 0.5 (the aspect ratio of hemispheres) by ≈ 3.6 ML.

Further supporting our analysis above, the data from ≈ 3.6 ML to ≈ 5.5 ML can be reasonably well fit with the hemispherical-cap model with particle densities of 3.4×10^{11} particles/cm² at 300 K and 5.4×10^{11} particles/cm² at 100 K, which are extremely similar to the values found at 2 ML for flat disks. From 0-1 ML, the aspect ratio ranges from ≈ 0.1 to 0.2, which is consistent with the findings of Benedetti et al.¹⁵² The aspect ratio appears to be nearly the same for both 300 K and 100 K across the entire coverage range, however this could be due to the aforementioned assumption that they are the same at 2 ML.

The particles' effective diameter (Figure 4.4(a)) increases very rapidly from 0 to 0.4 ML, and then levels off to remain essentially constant to ≈ 5 ML, with an average value of ≈ 7 nm above 0.4 ML (using points at both 100 K and 300 K). This result implies indicate that the Au particles reach a critical lateral size (effective diameter) of 7 nm by 0.4 ML, and continue to grow mainly in thickness, but very little in diameter at higher coverages, consistent with the increase in aspect ratio. Close inspection of Figure 4.4(a) reveals that the diameter appears to increase very slowly between 0.4 to ≈ 5.5 ML at 300 K, from ≈ 7 to ≈ 8 nm. At 100 K there is no measurable increase outside the noise from the slightly lower average diameter of ≈ 6.5 nm above 0.4 ML.

Finally, knowing a and R allows us to more precisely determine the thickness of the disks *without* any assumption of macroscopic shadowing area (given by $2aR$ per particle above). Using this relationship, the data in Figure 4.3 have been replotted in Figure 4.4(c). Although the general trend is similar to what was observed in Figure 4.3, the early-coverage points are even lower in thickness, and the high-coverage points are even higher. Additionally, the thicknesses at very low coverages (from 0-0.4 ML) average 0.45 ± 0.09 nm, which is within error equal to the thickness of two Au(100) atomic layers (0.407 nm). Au(100) layers are chosen rather than Au(111) here because this epitaxial relationship has been observed on MgO(100) and predicted by multiple

groups,^{58,137,157,159,169,204} although some have also observed Au growth with the (111) orientation,¹⁸¹ or a disordered Au structure that can rapidly change shape, as in quasi-melting.¹⁹⁸ The horizontal grey line in Figure 4.4(c) indicates the thickness of two Au(100) layers. That the early data falls on this bilayer thickness line agrees with our observation in the normalized LEIS data of Au particles potentially growing as 2D islands with bilayer thickness.

The morphology of Au on MgO at 300 K was also monitored with XPS using the integrated normalized intensities of the Au 4f_{5/2}, Mg 1s, Mg 2p, and O 1s signals as a function of Au coverage. The Mg 2p and Au 4f peaks were deconvoluted using the procedure described in ref.²⁰⁵ XPS is far less surface-sensitive than LEIS, and is therefore not as sensitive to changes in particle shape. It was used here only to verify general agreement. The data below 0.4 ML were well-described by a single-layer growth model for XPS (XPS is not sensitive enough to distinguish between single-atom-thick layers and bilayers), and above that coverage the data were fit well by both a flat-disk model with 3.0×10^{11} particles / cm² and a hemispherical-cap model with a particle density of 3.5×10^{11} particles / cm².

4.3.4 Heat of Adsorption at 300 K and 100 K

The calorimetric heats of Au atom adsorption on MgO(100) at 300 K and 100 K are shown as a function of total Au coverage in ML in Figure 4.5. These adsorption heats have been adjusted for the sticking probability of Au, to obtain the heat *per mole adsorbed*, as described above, as well as for the small translational energy difference between atoms emitted from the hot metal atom source and these same atoms in a Boltzmann distribution at the sample temperature (either 300 K or 100 K), as described previously.⁷² With these corrections, these reported heat data correspond to the standard molar enthalpy of adsorption with both the gas and the solid at the

temperature of the MgO(100) film (multiplied by negative one, so that exothermic values are presented as positive rather than negative, as is conventional in calorimetry).

At 300 K and 100 K, the initial heat of adsorption of Au on MgO(100) is 285 kJ/mol and 209 kJ/mol, respectively. As Au coverage increases, the heat of adsorption first increases rapidly, but then slowly levels off, reaching within 10 kJ/mol of the bulk heat of sublimation of Au(solid) (368 kJ/mol at 300 K, 363 kJ/mol at 100 K¹⁸) by ≈ 2 ML for both temperatures. The lower value of initial heat at 100 K compared to 300 K is likely due to a higher fraction of Au atoms adsorbing to terrace sites rather than stronger-binding step and corner sites that are accessible at 300 K, due to slower Au adatom diffusion at 100 K (see Discussion). Most late transition metals that are vapor-deposited on oxides bind preferentially at steps and kink sites / corners when the temperature is high enough for the adatoms to diffuse to the steps,^{42,138,206} and this was found to be the case for Au on MgO(100) in both DFT calculations^{158,207} and experiments at temperatures above 300 K.^{137,165,169,170,197,198}

The lineshape of the Au mass spectrometer signal versus time for the atoms that did not stick was analyzed at both 300 K and 100 K. It is indistinguishable from the line shape generated by the Au atoms that desorb during zero-sticking measurements, which essentially measures the instrument response function of the mass spectrometer signal versus time as the beam pulse ends. This indicates that the incoming Au atoms that adsorb onto MgO(100) but do not stick must desorb with a surface residence time, τ , that is < 10 ms, which is the time resolution of this measurement. If we assume that the atoms that do not stick permanently are indeed transiently adsorbed as monomers, this means that their desorption rate constant, $k_d = 1/\tau$, is $> 100 \text{ s}^{-1}$. By assuming a prefactor for the desorption rate constant of 10^{13} s^{-1} , this lower limit on the rate constant implies that the desorption activation energy for Au monomers on MgO(100) must be below 64 kJ/mol at

300 K, and below 22 kJ/mol at 100 K. These values are substantially smaller than the initial heats of adsorption on Figure 4.5 of 285 and 209 kJ/mol at 300 K and 100 K, respectively.

4.4 DISCUSSION

4.4.1 Comparison to DFT Calculations for Au Monomers

DFT calculations predict Au monomer adsorption energies onto the regular terrace sites of MgO(100) ranging from 52-96 kJ/mol^{158,207–212} (where the Au atom is positioned on top of an oxygen anion, which has been confirmed experimentally to be the preferred terrace binding site for Au adatoms²¹³). The upper limit on the Au monomer's surface residence time measured above sets an upper limit on the desorption activation energy for Au monomers on MgO(100) of <64 kJ/mol at 300 K, and <22 kJ/mol at 100 K. While the value at 300 K falls within the range of DFT adsorption energies, the value at 100 K is significantly lower. The value at 100 K of <22 kJ/mol is consistent with the 300 K limit of <64 kJ/mol, only more restrictive. This 100 K limit of <22 kJ/mol is more likely to represent Au binding at terrace sites, since Au atoms might diffuse to sample defects at 300 K. Del Vitto et al.²⁰⁷ calculated a 40% (36 kJ/mol) larger binding energy for an Au monomer on a MgO(100) step compared to on top of a terrace oxygen.

4.4.2 Comparing Morphology to Previous Studies

The LEIS results of Figure 4.4(c) indicate bilayer island growth in the first 0.4 ML. Blick et al.¹⁶² saw two-dimensional Au rafts in TEM images of Au/MgO powder catalysts formed by wet impregnation. These rafts were the dominant form of Au at low loadings. In simulations of cluster geometry on the MgO(100) surface using many-body potentials based on first-principle calculations, Ferrando et al.¹⁵⁹ found that for 30-atom clusters, FCC(001) bilayers are nearly degenerate with the global minimum shape of square pyramids. Even if 2D islands are not

thermodynamically preferred, their growth could occur due to kinetic effects.^{42,214} Recently, it was predicted first by DFT²¹⁵ and then confirmed by experiment²¹⁶ that when MgO(100) films grown on Ag(100) are thinner than 8 layers (≈ 1.6 nm), Au grows exclusively as 2D islands. This last example is likely the effect of an interaction between Au and the underlying substrate, which our MgO(100) films are thick enough to eliminate since they are ≈ 3.5 nm thick.

The growth of 2D metal islands at low coverage was also reported in our previous work for Cu⁷⁴ and Ag⁶⁷ on MgO(100), where the normalized AES signals were fit well by a layer-by-layer growth model below 0.3 ML. Since AES is far less sensitive than LEIS, those measurements were likely unable to distinguish between monolayer and bilayer islands in this regime.

Given the strong initial heats of adsorption measured here and the formation of large-diameter 2D bilayer islands, it is surprising that the O and Mg LEIS signals are strong in LEIS at very high Au coverages (>60 ML). In contrast, in our group's experiments for Ag on MgO(100), the O signal in AES was no longer visible above 30 ML Ag coverage,⁶⁷ despite the larger probe depth of AES compared to LEIS. This result supports our observation that once a critical two-dimensional diameter of ≈ 7 nm has been reached, the Au particles exclusively thicken at nearly fixed diameter (Figure 4.4(a)), getting very thick (up to ≈ 4 -5 nm) but never entirely covering the MgO(100) substrate. Once again, this phenomenon may occur because the binding of single Au monomers to MgO(100) terraces is so weak that the Au atoms diffuse readily to find a nearby large Au particle, where their binding is apparently preferred when they step-up onto the topmost plane. Del Vitto et al.²⁰⁷ calculated a very low value for the single Au atom diffusion barrier on the MgO(100) surface of ≈ 0.2 eV, and Metois et al.²¹⁷ observed extremely mobile Au adatoms on cleaved MgO(100) surface at 300 K. A growth model in which islands thicken without getting

wider can occur for kinetic reasons,²¹⁴ and may also occur due to the buildup of strain with increasing island size due to lattice mismatch.^{78,148}

4.4.3 Variation of the Heat of Au Adsorption with Au Nanoparticle Size

Next the calorimetric data versus the geometric parameters of the particles formed, such as thickness and effective diameter, is replotted. To get a continuous relationship between thickness t and coverage Θ , the data at both 300 K and 100 K in Figure 4.4(c) were fit to a modified exponential of the form $t = A(1 - \text{EXP}(-B\Theta))^C$, as shown by the dashed lines in red and blue for 300 K and 100 K, respectively.

The heat versus coverage data of Figure 4.5 are replotted versus the resulting thickness in Figure 4.6. The thicknesses for the first 10 to 20 data points of the heat curves in Figure 4.5 fall below the thickness of one Au(100) atomic layer (0.203 nm), which is unphysical. Therefore, the early coverage points were forced to equal the thickness of two Au(100) layers based on the LEIS evidence that Au is forming bilayers. The heat increases with thickness, approaching within 10 kJ/mol of the bulk heat of sublimation by a thickness 3.2 nm.

In the low-coverage range, these data in Figure 4.5 represent the heat of adsorption of Au on 2D Au bilayer islands at constant thickness such that the 2D islands are changing only in their effective diameter. Their average diameter at each coverage is estimated here by first determining the average number of atoms in each particle (based on the coverage and the best-fit particle density), and then by assuming these particles have the density of bulk Au(solid) and the thickness of a Au(100) bilayer in bulk Au(solid) (i.e., 0.406 nm). The Au heat of adsorption versus the resulting 2D Au island diameter in this constant-bilayer-thickness regime is shown in the inset of Figure 4.6. On the top axis of this inset is also shown the average number of atoms per particle,

which is proportional to the square of the diameter. This is the first time the heat of adsorption has been measured as a function of 2D particle diameter for any metal on any oxide surface.

The data in Figure 4.6 present the *differential* heats of adsorption as a function of particle size, which directly reflect differences in the chemical potential of the metal atoms, but with opposite sign, as described in References ¹²⁷ and 56. In brief, entropic contributions to the free energy are small compared to the large changes in enthalpy measured here, therefore these entropic contributions can be neglected, and the chemical potential of a metal atom in a particle of diameter D , $\mu(D)$, relative to that of the bulk metal, $\mu(\infty)$, (set as the reference zero here) is the heat of sublimation of bulk Au minus the differential heat of Au adsorption at diameter D . Thus, another way to view the data from Figure 4.6 is to plot the chemical potential versus average effective particle diameter (or particle thickness), which is shown on the right-hand axes of Figure 4.6. When evaluated in this way, 1.3 nm diameter bilayer Au islands are ≈ 82 kJ/mol higher in chemical potential than those that have reached the bulk size limit (>7 nm in diameter and >2.5 nm thick). Additionally, atoms in 1.3 nm diameter 2D islands at 100 K are ≈ 69 kJ/mol higher in chemical potential than 1.5 nm diameter 2D islands at 300 K (due to the difference in Au particles nucleated at defects at 300 K versus terraces at 100 K, see below). This difference in chemical potential reflects the thermodynamic driving force for catalysts to sinter into larger particles with time on stream.^{39,56,127} It also shows why maintaining gold nanoparticles at their small size is challenging, and it reflects a decreasing propensity for the metal to bind strongly to small adsorbates.⁵⁶

Finally, the heat of adsorption and corresponding chemical potential of Au atoms in Au particles versus the number of atoms per particle is shown (as determined above) over a larger coverage range without an assumption of particle geometry at 300 K and 100 K in Figure 4.7. These two datasets converge at particle sizes above ≈ 1400 atoms. Interestingly, Ferrando et al.¹⁵⁹

calculated that above 1200 atoms, Au particles cross over from FCC(001) geometry to the Au bulk-preferred FCC(111). The convergence in the heat data suggests that once particles reach 1400 atoms, they are spread across such a large area of the MgO(100) surface that the incoming adatoms that attach to the particle no longer experience any significant energetic difference between attachment to a particle nucleated on a terrace and one at a defect. This value of 1400 atoms seems to coincide well with the point at which these nanoparticles are beginning to reach a size that resembles their stable bulk properties.

4.4.4 The Effect of Temperature on Adsorption Energy: The Role of Defects

It was proposed previously in this chapter that the heat data at 100 K include more contributions from Au binding at terrace sites than the heat data at 300 K. To examine this, the heat of adsorption of Au on MgO(100) at 300 K is compared to that at 100 K for the smallest common particle size that is measured at both temperatures. At 300 K, the initial Au heat of adsorption (285 kJ/mol) corresponds to Au particles that contain ≈ 31 atoms. In contrast, the heat of adsorption of Au at the same particle size of 31 atoms at 100 K is only 217 kJ/mol, 68 kJ/mol lower than at 300 K. This large difference in the temperature-dependent adsorption energies on MgO(100) can only arise if these Au particles are at different sites. The fact that the adsorption energies are so dramatically lower at 100 K – where there is less thermal energy for Au atom diffusion – indicates that these measurements at 100 K are due to Au particles at weak-binding terraces, while at 300 K they are from Au particles that were thermally able to nucleate at the stronger-binding defects, which was enabled by the faster diffusion of Au particles at 300 K.

4.4.5 Adhesion Energy of Au on MgO(100)

The adhesion energy of nanoparticles onto a flat surface, E_{adhesion} , can be found from the integral heat of adsorption and the morphology measured in LEIS using a thermodynamic cycle described in detail in Reference ⁴² and Chapter 3, giving the following relationship (Equation 3.1):

$$n \sum_n \Delta H_{\text{ads}} = -n\Delta H_{\text{sub}} + A[(1 + f)\gamma_{\text{v/m}} - E_{\text{adh}}]$$

where $\gamma_{\text{v/m}}$ is the surface energy of the bulk nanoparticle material, f is the surface roughness factor, $\sum_n \Delta H_{\text{ads}}$ is the integral molar heat of adsorption up to the coverage of interest, n is the number of moles of the adsorbate on the surface at that coverage, A is the total area covered by the metal, and ΔH_{sub} is the bulk heat of sublimation of the adsorbate.

For particles, this method is typically applied to the large-particle limit, which is the highest coverage where no more than $\approx 35\%$ of the surface is covered by the adsorbate (as determined by LEIS).⁶⁷ (At higher coverages, particles may start to overlap, after which their size can no longer be estimated.) For Au on MgO(100), the normalized LEIS signals do not reach 35% coverage until ≈ 5.5 ML, which is in the region where these particles are approximately hemispherical. This method of determining adhesion also requires us to know the surface roughness factor at the point where adhesion is determined. When the Au particle geometry is changing at any given coverage, the roughness factor changes with it. For instance, for a continuous, atomically-smooth adsorbate layer, the roughness factor is 1; for hemispherical caps it is 2; and for flat disks with $a = 0.3$ (as seen with STM at 2 ML¹⁸¹), the roughness factor is 2.2.

At 300 K, the integrated heat at 2 ML along with measured particle density of 3.0×10^{11} particles/cm² assuming flat disks with this same STM aspect ratio (i.e., $a = 0.3$, for which $f = 2.2$) gives an adhesion energy of 2.24 J/m². These disk-shaped particles are ≈ 8.1 nm in diameter and

≈ 2.4 nm thick at this coverage, according to this model. If the value of Au / MgO(100) adhesion is lower than the Au / Au adhesion energy – which is simply twice the Au surface energy – this indicates that Au favors forming 3D clusters rather than wetting the surface. Using the value of 1.51 J/m^2 for the Au(111) surface energy,¹⁴⁹ assuming that once these disk-shaped Au particles reach this size, they adopt their preferred 111 interface, then the Au / Au adhesion energy is 3.02 J/m^2 . This value is indeed larger than the range of Au / MgO(100) adhesion energies measured here at 300 K, consistent with our observation of the formation of 3D particles at high coverages. The formation of 2D bilayer islands at low coverage thus seems to be due to a kinetic limitation in this case, rather than a thermodynamic preference, since the heats of Au adsorption measured here at low coverage are far lower than on large 3D particles. Kinetically-driven 2D growth is common,^{42,214} and has been observed for Ag on MgO(100).²¹⁸

An important role of defects on the adhesion energy can be seen by comparing the adhesion energy at 300 K to the corresponding value at 100 K, where defects are less populated due to slower metal monomer diffusion.^{42,134,138,165,206,219} By using the same coverage region (up to 2 ML) and roughness factor discussed above at 300 K, a similar analysis of the calorimetry data at 100 K gives an adhesion energy of 0.31 J/m^2 at 100 K for 6.7 nm diameter disk-shaped particles. To compare particles of similar size, the adhesion energy of ≈ 7 nm particles at 300 K (assuming the same shape and aspect ratio as the value 2 ML coverage found above for 8.1 nm particles), is 1.81 J/m^2 , which is nearly 6x larger. Combined with the evidence presented above for particle-size dependent adsorption energies that depend on temperature, these very different adhesion energies at 300 K and 100 K further confirm that at 100 K, the adsorption and adhesion energies of Au particles on the terraces of MgO(100) is being measured, while at 300 K, the adsorption and adhesion energies are from large Au particles at defects. While this instrument does not have the

ability to directly visualize the binding sites of Au particles using calorimetry, the combined spectroscopic and calorimetric results presented here suggest that the work presented here represents measured information about the binding strength of large Au particles at defects at 300 K and on terraces at 100 K.

The calorimetric adhesion energy of ≈ 7 nm diameter disk-shaped Au particles on MgO(100) measured here at 300 K (1.81 J/m^2) is much higher than the values determined at 300 K using TEM particle-shape measurements for 2-6 nm diameter Au particles of on MgO(100), which was only $0.45\text{-}0.67 \text{ J/m}^2$.^{56,75,76} However, the calorimetric adhesion energy of 0.31 J/m^2 at 100 K for ≈ 7 nm diameter disk-shaped particles agrees *far* better with these values determined from TEM particle shapes. Importantly, in these TEM measurements, the Au particles that were analyzed appear to be at terraces with no morphological defects present.^{75,76} Thus, it makes sense that the 100 K calorimetry value, which is also at terraces, should agree better with these TEM measurements at terraces than the 300 K calorimetry value, which is attributed to particles at defect sites instead (probably step edges). These lower values found with TEM at 300 K and by calorimetry at 100 K also agree significantly better with DFT calculations of the adhesion energy of 1-2 layers of Au on MgO(100) terraces ($0.16\text{-}0.42 \text{ J/m}^2$).¹⁸⁹

Other possible reasons why the calorimetric adhesion energy for Au on MgO(100) at 300 K is much larger than that at 100 K and that from TEM particle-shape analysis (for particles on terraces at 300 K) can easily be ruled out. The calorimetric values were measured here on MgO(100) films that ranged from 2 to 5 nm thick, which was thick enough to reach the bulk-thickness limit for Ag on CeO₂(111).⁷⁰ Therefore, it is unlikely that they were affected by significant interaction from the underlying Mo(100) substrate. Furthermore, our oxidizing preparation conditions make it highly unlikely that enough oxygen vacancies are present to affect

the heats, also supported by the absence of vacancy-related signal in the XPS spectra. This is important because oxygen vacancies bind Au adatom 210-300 kJ/mol more strongly than terrace sites on MgO(100).^{160,189,190,207,209} The only reasonable explanation for the difference in our adhesion energy at 300 K relative to that at 100 K or from TEM is the role of step edges or other surface morphological defects on our calorimetric adhesion energy here at 300 K.

This is the first direct comparison between adhesion energies measured by calorimetry and this same quantity measured using a different technique (TEM). While the value measured by calorimetry at 300 K differs greatly from that measured by TEM at 300 K, the disagreement is due to the effect of step edges on the calorimetric value at 300 K. Indeed, the value measured by calorimetry at 100 K for Au particles on terraces agrees well with that measured by TEM at 300 K, also for Au particles on MgO(100) terraces. Our calorimetric measurements reveal that the energy of Au nanoparticles on MgO(100) is highly sensitive to morphological defects such as steps, corners, and kinks, where they bind much more strongly than at terraces. Recently, morphological defects such as the “reverse corner” have been proposed to explain the electron-transfer properties of MgO(100) films that had previously been attributed to oxygen vacancy defects.^{195,196} The thermodynamic cost to form an oxygen vacancy on an MgO(100) terrace is extremely high (5-10 eV),^{220–222} and in most cases they are not present in large enough concentrations to effect observed results. In contrast, morphological defects, as well as those with higher dimensionality such as grain boundaries, have been observed experimentally in much higher concentrations. These defects can act as efficient electrostatic traps in thick MgO films, and Au has been observed to nucleate on these defects and grain boundaries.¹⁹⁴ Since Au is characterized by its high electronegativity, the very strong binding measured for Au at these types of defects may be due to their electron-rich character.

4.5 CONCLUSIONS

The heat of Au adsorption onto MgO(100) versus Au island diameter is measured here for coverages below 0.4 ML, where the Au grows as flat 2D islands of bilayer thickness. This is the first time the heat of adsorption has been measured as a function of 2D particle diameter for any metal on any surface. Intensities in LEIS versus coverage showed that at both 300 K and 100 K, Au grows on MgO(100) first as 2D bilayer islands up to ≈ 0.4 ML coverage, where their diameter grows with coverage until they reach an average diameter of ≈ 7 nm at 300 and 100 K. At ≈ 0.4 ML, these islands suddenly stop growing in diameter, and instead thicken with coverage. Using details of the Au particle shape and aspect ratio found at 2 ML Au coverage in the STM work of Benedetti *et al*¹⁵² at 300 K, the Au particle density was determined to be 3.0×10^{11} particles/cm² at 300 K, and slightly larger (5.2×10^{11}) at 100 K due to slower adatom diffusion. At 300 K, the Au heat of adsorption for particles containing 31 atoms is 285 kJ/mol, while at 100 K it is 68 kJ/mol lower, indicating that the measurements at 100 K are from Au particles at weak-binding terraces, while at 300 K they are from Au particles that nucleate at stronger-binding defects. An analysis of the lineshape of the Au mass spectrometer signal for nonsticking atoms provides an upper limit for the desorption activation energy for Au monomers on MgO(100) of 64 kJ/mol at 300 K, and 22 kJ/mol at 100 K. The adhesion energy of Au particles on MgO(100) at 2 ML Au coverage was determined using the particle shape and roughness factor described by Benedetti *et al.*¹⁵² At 300 K this value for 7 nm particles is 1.81 J/m², while at 100 K it is 0.31 J/m². The value at 100 K agrees far better with adhesion energy measurements found on this system using particle-shape techniques, which supports the conclusion that the adhesion energy at 100 K is for Au particles nucleated on MgO(100) terraces, while the much larger value at 300 K is due to particles at step edges and kinks, or other defects.

4.6 FIGURES

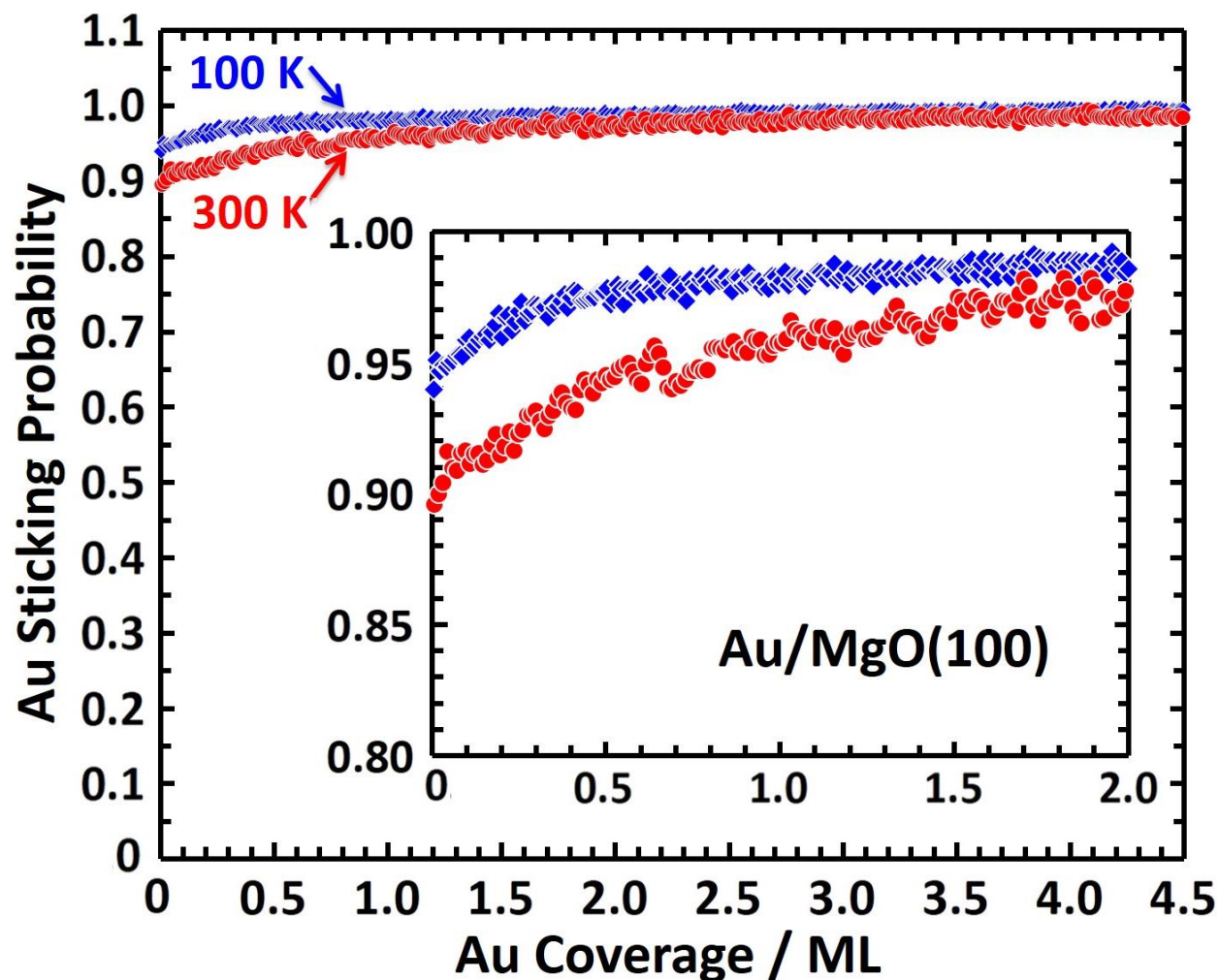


Figure 4.1. Measured sticking probability of Au atoms on MgO(100) as a function of total Au coverage in ML at 300 K (red circles) and 100 K (blue diamonds). The data at each temperature represent the average of three runs. The sticking probability starts at 90% at 300 K, 95% at 100 K, and reaches unity sticking by ≈ 2 ML at both temperatures. The inset shows the region from 1-2 ML in detail.

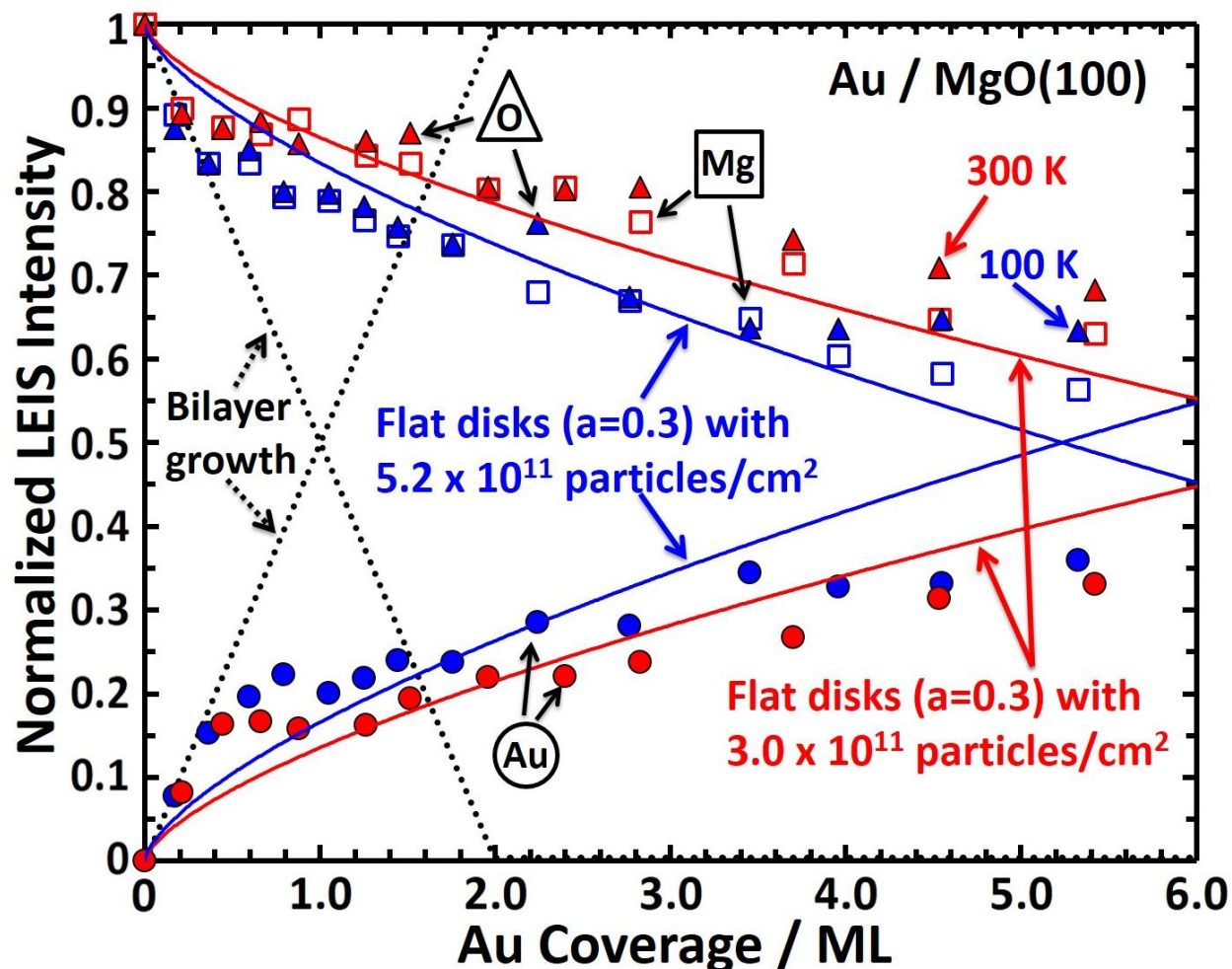


Figure 4.2. Integrated LEIS signal intensities for Au (closed circles), O (closed triangles), and Mg (open squares) as a function of total Au coverage on MgO(100). Data at both 300 K (red) and 100 K (blue) are shown. The substrate signals are normalized to the clean MgO(100) film, while the Au signals are normalized to the final Au coverage point scaled by the average of the remaining Mg and O signals to represent a thick Au overlayer covering the substrate. For Au coverages of 40-60 ML, $\approx 25\%$ of the Mg and O was typically still visible in LEIS. The black dashed lines correspond to the normalized LEIS signal expected from a bilayer growth mechanism. The solid red (300 K) and blue (100 K) line correspond to Au growing as flat circular disks with a fixed aspect ratio of 0.3 and a fixed particle density that is fit to the data at 2 ML. This particle density that best fits the 2 ML data is 3.0×10^{11} particles/cm² at 300 K and 5.2×10^{11} particles/cm² at 100 K.

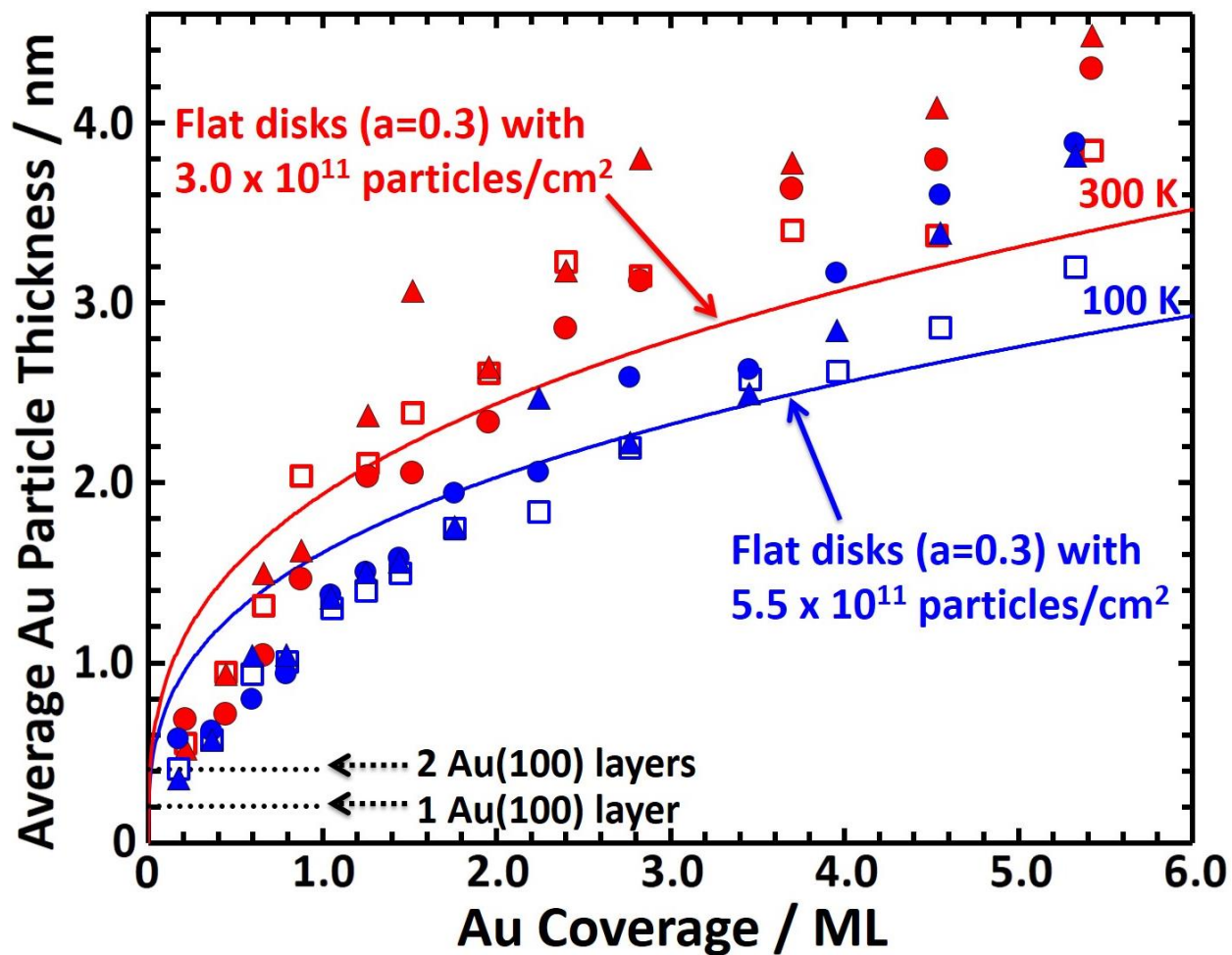


Figure 4.3. Average Au particle thickness versus Au coverage as measured by LEIS assuming flat circular disks with a constant number density determined by fitting Figure 4.2 at 2 ML with the STM-measured aspect ratio, and assuming a constant macroscopic shadowing factor of 1.382. These thicknesses were found using the Au, O, and Mg LEIS data from Figure 4.2 (using the same symbols). The solid curves are the expected result from the same flat-disk, fixed-aspect-ratio model and particle number densities shown in Figure 4.2. Using this representation, the failure of this fixed-aspect-ratio model is clear – Au particles are *thinner* than this model predicts at low coverages and *thicker* at high coverages, i.e., their aspect ratio is constantly increasing with coverage above ≈ 0.3 ML.

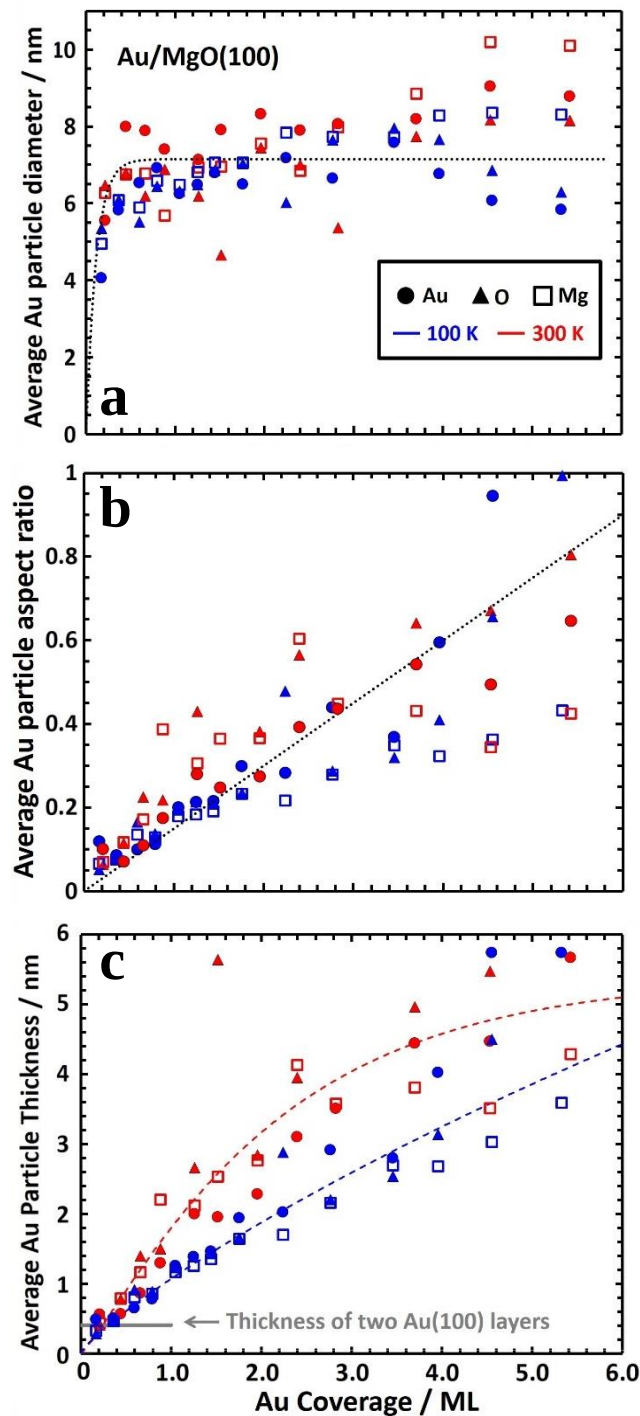


Figure 4.4. Average Au particle a) diameter and b) aspect ratio calculated concurrently from the total quantity of Au deposited and the fractional Au coverage as determined by the normalized LEIS signals from Figure 4.2 for Au (closed circles), O (closed triangles), and Mg (open squares) at 300 K (red) and 100 K (blue). These two Au particle parameters were determined from each LEIS point by assuming that the particle density remains constant at all coverages, and is equal to the best-fit values at 2 ML for 300 K and 100 K from Figure 4.2. The black dotted lines are shown to guide the eye, and indicate that Au particles increase rapidly in diameter from 0-0.4 ML, after which they grow thicker but with constant diameter from 0.5-3 ML. The aspect ratio increases nearly linearly with coverage above 0.5 ML at both temperatures. c) Real average Au particle thickness determined using the total amount of Au deposited, the aspect ratio, and the diameter at each point, using a macroscopic shadowing factor that is determined by the aspect ratio at each point. Compared to Figure 4.3, the low-coverage points are even thinner and the high-coverage points even thicker than the constant-aspect-ratio model predicted. Using a varying aspect ratio reveals that the first several coverage points lie at the thickness of an Au(100) bilayer. The dashed red and blue lines correspond to exponential fits to the 300 K and 100 K data, respectively, to map Au coverage to average particle thickness.

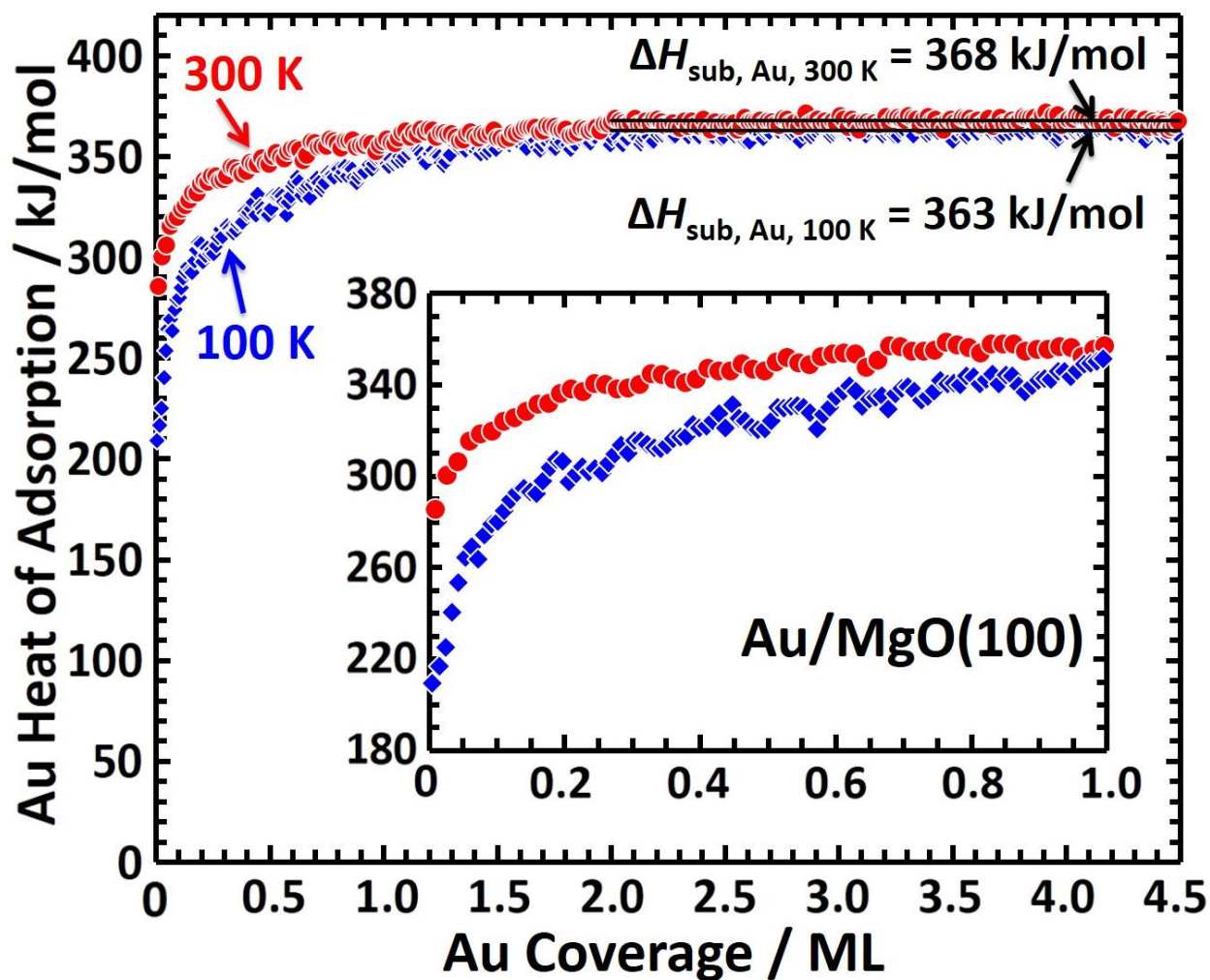


Figure 4.5. Heats of Au atom adsorption on MgO(100) at 300 K (red circles) and at 100 K (blue diamonds) as a function of total Au coverage (1 ML = 1.12×10^{15} atoms/cm²). The inset expands the range from 0-1 ML where the heat changes most rapidly with coverage.

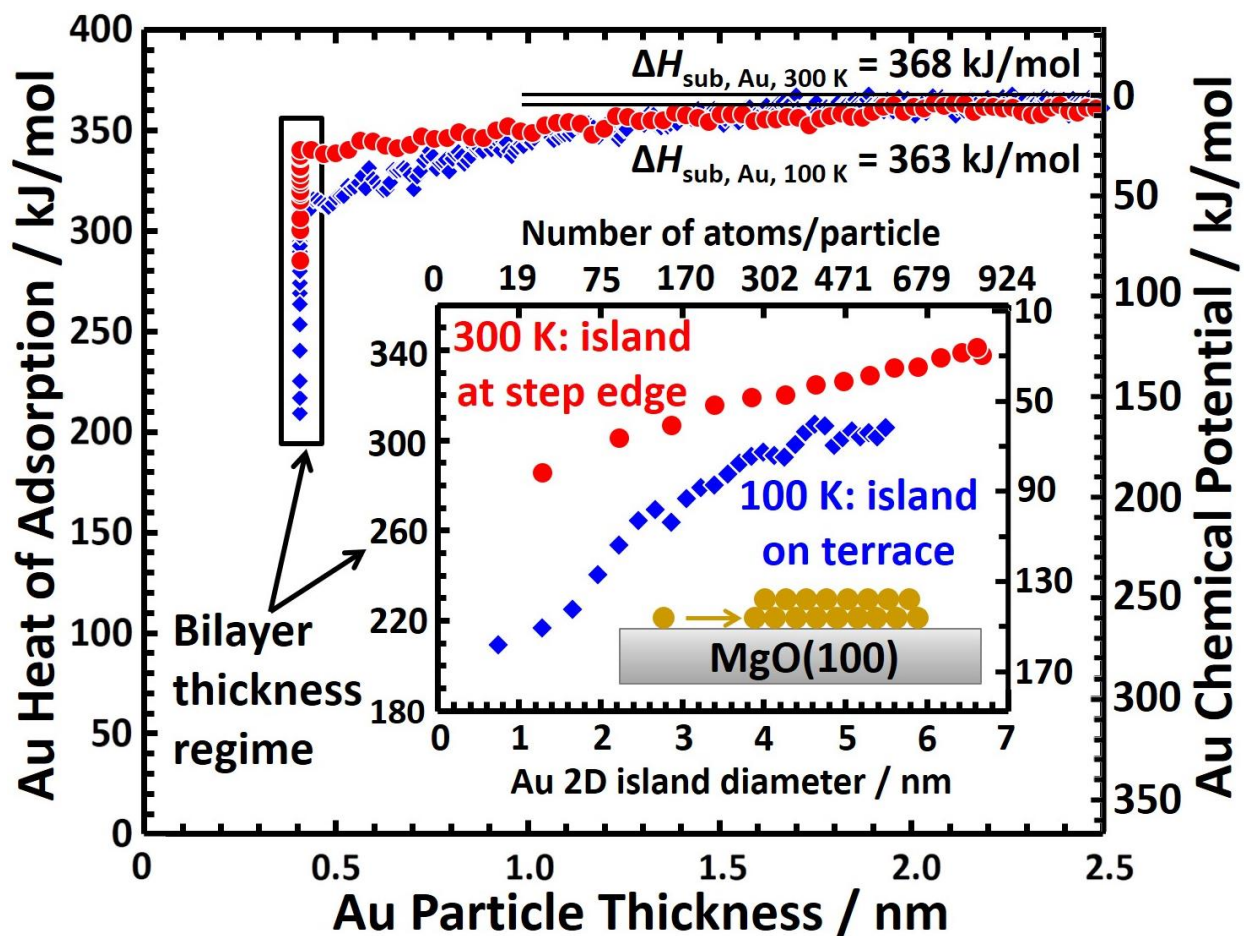


Figure 4.6. Au heat of adsorption (left axis) and the chemical potential of Au atoms in Au nanoparticles (right axis) versus average Au particle thickness, which is obtained from total Au coverage using the exponential fits to the data in Figure 4.4(c). Data that falls below the thickness of one Au(100) bilayer (0.407 nm) is forced to this thickness. This is done rather than forcing data to a single-layer thickness due to the LEIS results, however it may be possible that some of these very early data points are from single-layer islands. The inset shows the heat and chemical potential data in this 2D-island region as a function of 2D island diameter, which is obtained from the best-fit particle density found in Figure 4.2 and assuming bilayer thickness. The data at thicknesses above this 2D-island range show the effect of particle thickness at constant particle diameter of $\approx 7 \text{ nm}$.

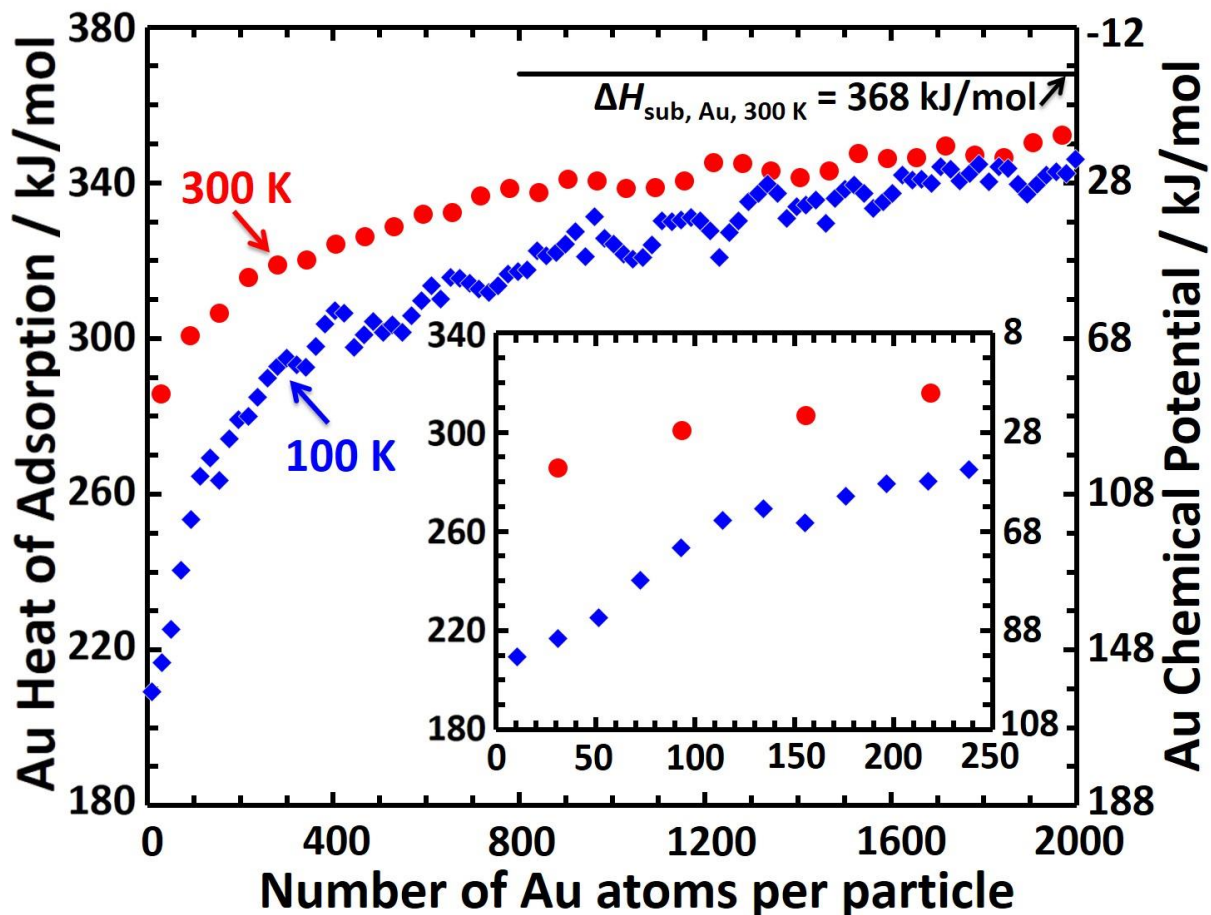


Figure 4.7. Au heat of adsorption (left axis) and chemical potential of Au atoms in Au nanoparticles (right axis) at 300 K (red circles) and 100 K (blue diamonds) plotted versus the number of Au atoms per Au particle as determined from the total Au coverage at each point, assuming a constant particle density at the values found in Figure 4.2 (3.0×10^{11} particles/cm² at 300 K, 5.2×10^{11} particles/cm² at 100 K). The smallest number of atoms per particle is 10 for 100 K and 31 for 300 K. The heat data (and therefore chemical potential) for these temperatures are different at similar particle sizes due to the much lower rate of diffusion of Au atoms at 100 K, so that more Au particles occupy the less favorable terrace sites on MgO(100) at 100 K, whereas they grow at the more stable step edges at 300 K. However, as these particles grow larger, the heats converge by the time they reach ≈ 1400 atoms, at which point these particles are large enough that the majority of the heat of adsorption comes from the formation of Au-Au bonds within the particle, with little influence from the bonding to the oxide below.

Chapter 5. Adsorption and Adhesion of Cu on Reduced CeO₂(111) Surfaces at 300 and 100 K

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The morphology and interfacial energetics of vapor-deposited Cu on CeO_{2-x}(111) surfaces ($x = 0.05$ to 0.2) at 300 K have been studied using single-crystal adsorption calorimetry (SCAC), He⁺ low-energy ion scattering spectroscopy (LEIS), X-ray photoelectron spectroscopy (XPS), and low-energy electron diffraction (LEED). The changes in LEIS and XPS signals with Cu coverage indicate that Cu grows as 3-dimensional nanoparticles with a density of $\approx 8 \times 10^{12}$ particles/cm² on CeO_{2-x}(111) (where $x = 0.05, 0.1$ and 0.2). The initial heat of adsorption of Cu onto CeO_{2-x}(111) decreased from 300 to 272 and finally 257 kJ/mol as the extent of reduction increased from $x = 0.05$ to 0.1 and 0.2 . This shows that stoichiometric ceria adsorbs Cu more strongly than oxygen vacancies, consistent with prior calculations. On CeO_{1.95}(111), the heat dropped quickly with coverage in the first 0.1 ML (1 ML = 7.9×10^{14} Cu atoms/cm²), attributed to nucleation of Cu clusters on stoichiometric step sites first, followed by the Cu particles spreading onto less favorable sites (step vacancies and terraces) as they grow in diameter. Above ≈ 0.1 ML (i.e., >0.8 nm in particle diameter), the Cu adsorption energies showed no variation with extent of ceria reduction: On all three surfaces, the heat of adsorption increased slowly with coverage (particle size) due to

the formation of more Cu-Cu bonds per adatom as the size grows, finally approaching the heat of sublimation of bulk Cu (337 kJ/mol) by 3.5 ML (2.5 nm size). The adhesion energy of Cu(solid) to CeO_{1.95}(111) was found to be 3.52 J/m² for 2.2 nm diameter particles, decreasing slightly with extent of reduction. The Ce 3d XPS lineshape showed an increase in Ce³⁺/Ce⁴⁺ ratio upon Cu adsorption, corresponding to the donation of at most ≈ 0.17 and 0.06 electrons per Cu atom to CeO_{1.95}(111) and CeO_{1.8}(111), respectively.

5.1 INTRODUCTION

The interaction of metal nanoparticles with their underlying oxide support can greatly influence catalytic properties such as long-term sinter resistance, activity, and selectivity. Specifically, the strength of bonding of the metal to the oxide support has been shown to control the chemical potential of the metal atoms in the nanoparticles and how it varies with particle size.^{39,52,56,57} This chemical potential in turn influences how strongly adsorbed catalytic reaction intermediates bind to the metal particles⁵⁶ and how quickly the particles deactivate by sintering.^{35,39} Thus, understanding the strength of bonding of late transition metals to oxide support and the resulting metal chemical potential is crucial for understanding structure – function relationships in catalysis. To improve our understanding of how the choice of metal and support can influence catalytic properties, detailed studies of model systems – where metal atoms are vapor deposited onto single crystal oxide supports – are often employed. With these model systems, the structure of the support surface, the size of the metal particles, and surface cleanliness can be better controlled.^{49,53,55,223} Here, this approach is applied to study model Cu / CeO₂ catalysts consisting of Cu nanoparticles grown by vapor deposition on CeO₂(111) surfaces with controlled extents of reduction.

Furthermore, prior to publication of work contained in this chapter, no one had previously reported an experimental measurement of the adsorption energy of any late transition metal adsorbed in the form of isolated atoms on any oxide surface. Also presented in this chapter are calorimetric measurements of the adsorption energies of Cu atoms onto CeO₂(111) under conditions where they remain as isolated adatoms on terraces and where they grow as Cu nanoparticles with controllable average size. From these the chemical potential versus particle size is estimated across the full range from single Cu adatoms to the bulk Cu(solid) limit. This has never been reported for any late transition metal on any oxide surface and provides a simple benchmark for validating the energy accuracy of quantum mechanical calculations of metal/oxide bonding, e.g., density functional theory (DFT).^{224,225} These Cu/CeO₂(111) model catalysts address the crucial role of ceria as a support^{31,35,39,48,102,126,150,151,226–233} and of Cu nanoparticles in industrial catalysis.^{234–236}

The energies of the Cu atoms in this system are studied using SCAC at both 300 K and 100 K. The Cu nanoparticle morphology is characterized using ion scattering spectroscopy (LEIS), and X-ray photoelectron spectroscopy (XPS). Adsorption energies are measured using SCAC along with detailed adsorbate structural studies at these temperatures to determine metal adhesion energies to various single-crystal ceria surfaces. This is important since differences in the metal's adhesion energy affect the sintering rates of these metal/support systems: the larger a metal's adhesion energy is to the support, the more resistant the metal is to sintering.³⁹ Cooling to 100 K enables production of isolated Cu adatoms located on stoichiometric CeO₂(111) terraces, while at 300 K Cu makes clusters at step edges even at the lowest coverage studied. XPS is also used to determine the electronic properties of both supported Cu nanoparticles and the reduced CeO₂(111) surfaces at 300 K. The results presented here help clarify the nature and strength of binding at the

Cu nanoparticle / ceria interface, how it depends on the extent of ceria reduction, and how interfacial bond strengths in general are influenced by the choice of metal and support. The results at 300 K are compared to similar measurements of Cu adsorption on MgO(100)^{64,74} and Ag adsorption on the same reduced CeO₂(111) surfaces.^{39,70} The results at 100 K are compared to previous DFT+U studies of the adsorption energy of Cu atoms on stoichiometric and reduced CeO₂(111) surfaces.^{31,48,150,151,227}

Copper supported on ceria has shown promise as a catalysts for a variety of reactions such as CO oxidation,^{237,238} water-gas shift reaction,^{239,240} and methanol synthesis.^{234,241} For methanol synthesis, the perimeter sites of copper nanoparticles at the interface with ceria were found to be the most catalytically active sites,²⁴¹ and Cu was only catalytically active when in the neutral form, rather than oxidized.²³⁴ However, few detailed structural studies exist for copper/ceria catalysts. One study by Szabová et al.²²⁸ of vapor-deposited Cu on CeO₂(111) showed that the oxidation state of Ce before Cu adsorption influenced the electronic structure of Cu nanoparticles, with oxygen vacancies donating electron density to Cu and stoichiometric sites withdrawing electron density from Cu.²²⁸ However, little was known about the strength of interfacial bonding and the structure of the adsorbed Cu in this system until this present report.

5.2 EXPERIMENTAL DETAILS

The CeO_{1.95}(111) thin films were grown on Pt(111) as described previously⁷⁰ in an adjacent UHV preparation chamber that is connected to the calorimetry chamber through a gate valve. The Pt(111) surface was cleaned by successive cycles of 1 kV Ar⁺ sputtering in 6 x 10⁻⁶ background Ar followed by annealing to 1173 K in UHV and then 873 K in 1 x 10⁻⁶ O₂ until no C was present in XPS and a sharp Pt(111) LEED pattern were observed. The CeO_{1.95}(111) films were grown via reactive evaporation of Ce in a 1 x 10⁻⁶ Torr O₂ background and a sample temperature of 873 K

with an average ceria deposition rate of 0.5 nm/min as determined from the attenuation of the Pt 4p_{3/2} photoelectron peak and the inelastic mean free path of Pt4p_{3/2} electrons escaping through CeO₂ calculated using NIST inelastic mean free path database (17.5 Å). Ceria oxidation state was measured by XPS and sample order was verified by LEED. Further reduced CeO_{1.90}(111) and CeO_{1.80}(111) samples were grown using the same procedure except by reducing the oxygen pressure to 1 x 10⁻⁷ Torr and tuning the resulting oxidation state by post annealing in 1 x 10⁻⁷ Torr O₂ until the desired oxidation state was achieved (usually 0.5-2 min).

The CeO_{2-x}(111)-coated Pt(111) sample was cooled to 100 K for calorimetry by mounting both the sample holder and the calorimetry detector head on a liquid nitrogen cooled thermal reservoir. Its temperature was monitored by two type-K thermocouples attached to the sample holder and the PVDF ribbon holder as close as possible to the Pt sample. Before each calorimetry measurement, the detector was retracted and the surface was flash-heated to 873 K (measured by optical pyrometry) in 1 x 10⁻⁶ Torr O₂ to remove adsorbed background gases. It re-cooled quickly (<3 minutes) to a stable temperature near 100 K, and calorimetry was begun. The Pt sample was mounted on a manipulator for XPS and LEIS analysis and transfer to/from the calorimetry position. The manipulator fork that holds the sample platen was cooled to 100 K by a reservoir of liquid nitrogen, and its temperature there was monitored by a type-K thermocouple mounted to the manipulator fork as close as possible to the sample.

The growth morphology of Cu on CeO_{2-x}(111) was determined using LEIS with a 135 degree scattering angle, 2 x 10⁻⁷ Torr He background, and 3 mA emission current which gives an ion current density of ≈90 nA/cm² averaged over the area that is rastered.

5.3 RESULTS

5.3.1 CeO_{2-x}(111) Thin Film Characterization.

CeO_{2-x}(111) thin films were grown in a separate preparation chamber on a 1 micron thick Pt(111) substrate to a thickness of 4 nm as described above. Our previous results for Ag adsorption on such CeO_{2-x}(111) thin films showed that thicknesses of 2, 3 and 4 nm were sufficient to give the same results (heats of Ag adsorption versus coverage), but differed from results for films that were only 1 nm.⁷⁰ Thus, the 4 nm thickness used here is certainly expected to give bulk-like ceria surface properties. Ceria film thickness was determined by measuring the attenuation of the Pt 4p_{3/2} XPS peak from the clean Pt(111) substrate using the inelastic mean free path of a Pt photoelectron of 17.5 eV kinetic energy escaping through a ceria overlayer. LEED images of the as-grown CeO_{2-x}(111) thin films gave sharp (1.4 x 1.4) patterns (not shown) as reported previously,⁷⁰ indicating the surface was well ordered. No Pt(111) LEED spots were visible for the 4 nm ceria films, but the (1.4 x 1.4) pattern and epitaxial relationship were confirmed by performing LEED on a thinner ceria films (0.5-1 nm) indicating an epitaxial relationship to the underlying substrate.

Figure 5.1 shows representative Ce 3d XPS for the three CeO_{2-x}(111) oxidation states studied here (where x = 0.05, 0.1 and 0.2). For CeO_{1.8}(111), a sample Shirley background and 10-peak decomposition (4 for Ce³⁺ and 6 for Ce⁴⁺) are shown. The peak positions and relative sizes of Ce³⁺ and Ce⁴⁺ peaks were taken from reference spectra reported for bulk Ce₂O₃ and CeO₂.¹²⁸ The CeO_{2-x}(111) film stoichiometry was determined by measuring the Ce³⁺ concentration in the Ce 3d XPS feature compared to the total integrated Ce 3d area (Ce³⁺/[Ce³⁺ + Ce⁴⁺]). Reduced CeO_{1.8}(111) films grown on Pt(111) have usually been prepared by high-temperature annealing in UHV.^{70,242} However, no change in oxidation state was observed when our as-prepared films were

annealed, but instead an increase in the Pt 4p_{3/2} XPS peak was observed when heated hot enough to see a significant change in the spectra beyond a reduction to CeO_{1.92}. Thus, either the as-grown ceria film dewetted from the Pt(111) surface to make thicker 3D particles upon annealing in UHV, or any Ce that was reduced subsequently disappeared into the Pt(111) bulk. Therefore, the reduced ceria films prepared for this study (CeO_{1.90}(111) and CeO_{1.80}(111)) are instead prepared by growth in a lower oxygen pressure than usual (1×10^{-7} Torr), which gives an approximate initial oxidation state of CeO_{1.60}. Annealing for 0.5 to 1 minutes at 873 K and 1×10^{-7} Torr O₂ oxidized the ceria film to CeO_{1.80}(111) and CeO_{1.90}(111) respectively. The calculated oxidation state is the same when measuring at emission angles of 45 and 90 degrees indicating the oxidation state on the surface is the same within the probe depth of XPS. Unfortunately, STM was not available to verify the defect density of the as-prepared CeO_{2-x}(111) films, however, Luches et al.²⁴² have shown that similar annealing of reduced CeO₂(111) films grown on Pt(111) in oxygen for short periods does not create additional step or kink sites compared to the original film. It is likely that no additional steps or kinks were introduced in the ceria films studied here by annealing in oxygen. Also, previous CeO_{2-x}(111) films grown on Pt(111) by Farmer et al.⁷⁰ using very similar preparation methods have been estimated to have a total surface defect density of 5-6% using STM. It is therefore estimated that the defect density is the same on the films studied here. For a detailed analysis on the surface defect structure see Reference 70.

5.3.2 Cu Sticking Probability on CeO_{2-x}(111) at 300 K and 100 K.

The sticking probability of Cu on CeO_{2-x}(111) was measured as the number of non-sticking Cu atoms in each pulse determined by the magnitude of the time-integrated transient QMS signal compared to the signal of a reference pulse from a hot Ta flag where no sticking occurred. At all

Cu coverages at both 300 and 100 K, the sticking probability was >0.99 for all three $\text{CeO}_{2-x}(111)$ films.

5.3.3 Cu Film Growth Morphology on $\text{CeO}_{2-x}(111)$ at 300 K.

The growth morphology of Cu on $\text{CeO}_{2-x}(111)$ was investigated using He^+ LEIS at 300 K and is shown in Figure 5.2. Discreet amounts of Cu were deposited onto $\text{CeO}_{1.95}(111)$ films at 100 K using the same Cu atomic beam as in the calorimetry experiments, and the integrated Cu and Ce signals were monitored using He^+ LEIS. Total Cu coverage is defined here in monolayers (ML) where $1 \text{ ML} = 7.89 \times 10^{14} \text{ atoms/cm}^2$, which is the density of O atoms in the top layer of $\text{CeO}_2(111)$. The integrated LEIS intensity of the Cu was normalized to that from a thick-enough Cu overlayer to block all the Ce signal ($>40 \text{ ML}$). The Ce LEIS signal was normalized to that for clean $\text{CeO}_{1.95}(111)$ before Cu deposition. When normalized in this way, the Cu signal is a direct measure of the fraction of the ceria surface masked by Cu particles and the Ce signal measures the fraction that is not masked. The Cu LEIS signal increases with Cu coverage and the Ce signal decreases for all Cu coverages, indicating Cu does not diffuse into the substrate, but rather forms a surface layer on $\text{CeO}_{2-x}(111)$.

The data in Figure 5.2 are compared to two mathematical growth models, the layer-by-layer and hemispherical-cap models. The data deviates markedly from the layer-by-layer model, indicating that Cu growth is not two-dimensional in the first layer. The data are well fit using the hemispherical-cap model described by Diebold et al.,¹³⁰ which has been modified to better describe macroscopic shadowing of the incident ion beam by hemispherical particles.¹³¹ It assumes that the film grows as 3D particles with the shape of hemispherical caps, with a fixed number density of particles, n , at all metal coverages, and that all particles have the same average diameter, D , at any one coverage. The fixed density of particles is a well-known consequence of particle growth

kinetics whereby a saturation density of clusters is formed at very low coverage and stays constant thereafter.¹³⁴ Since n and D are mathematically related for a given total Cu coverage, n is the only fitting parameter.¹³⁰ When the angle of detection is normal to the surface but the ions are incident at angle $\theta_i = 45^\circ$ from normal as here, that model gives that the fraction of the ceria substrate signal masked by Cu particles equals $n\pi D^2 (1 + 1/\cos\theta_i)/8 = (1.207)n\pi D^2/4$.¹³¹ It was determined for the data in Figure 5.2 from the best-fit line, which was generated using a least-squares analysis and gave a Cu 3D particle density of 7.8×10^{12} particles/cm² on both CeO_{1.95}(111) and CeO_{1.80}(111). No LEIS growth-mode data were collected for CeO_{1.90}(111), which was assumed to have a similar particle density as seen at the higher and lower oxidation states. The hemispherical-cap model has been shown to be a good model for many late transition metals supported on oxides of the type used as catalyst supports,²⁴³ and most late transition metals have been shown to grow as 3-dimensional particles on these oxides.⁵⁵

To ensure there was no sample damage due to He⁺ ion bombardment during the course of the experiments in Figure 5.2, a control experiment was run using only two coverages where the signals are very sensitive to coverage (≈ 1 and 4 ML) so much less total ion beam exposure up to 4 ML. The data from the two-point experiment (not shown) fell within error of the best-fit lines for each sample in Figure 5.2, indicating that sputter damage from the low dose of He⁺ ions did not significantly influence the data in Figure 5.2.

The normalized LEIS signals in Figure 5.2 directly provide the fraction of the ceria surface whose signal is masked by Cu particles, and the fraction of the total maximum Cu signal (due to complete coverage by Cu) that is observed at any given Cu coverage. Assuming that the actual footprint of the Cu particles is expanded due to macroscopic shadowing by the same factor as is the case for hemispherical caps at this LEIS measurement geometry (see above), these fractions

can be divided by 1.207 to estimate the area fractions actually covered by Cu particles, and not just masked by them from ion trajectories. Since the average Cu film thickness is known from the Cu coverage (assuming the Cu particles have the density of bulk Cu(solid)), it can be divided by this covered fraction for each LEIS data point (both Cu and Ce) to get the average particle thickness. Figure 5.3 shows the average Cu particle thickness versus Cu coverage for both ceria films estimated in this way from each LEIS data point. Since the average thickness of a hemispherical cap is 1/3 its diameter, this thickness is multiplied by 3 to show the corresponding average diameter along the right-hand axis here. For comparison, the result expected from the same hemispherical-cap model and particle number density as used for the best fit in Figure 5.2 is shown. The agreement is excellent.

The growth morphology of Cu on CeO_{1.95}(111) was also studied using XPS as shown in Figure 5.4. The integrated signal intensities of Cu 2p_{3/2} and Ce 3d XPS regions, normalized using the same method as the LEIS signals above, are plotted versus Cu coverage. The Cu data were fit using the literature electron mean free path at a kinetic energy of 554 eV (1.09 nm¹³⁶). The data were again well fit by the hemispherical-cap model as derived for electron spectroscopies¹²⁹ with the same particle density as used to fit the LEIS data (7.8 x 10¹² particles/cm²). Diebold et al.¹³⁰ showed that the mean free paths of electrons escaping from an ordered substrate is smaller than literature mean free paths due to forward focused electrons on the uncovered substrate that become attenuated by an overlayer due to blocking of the forward focused paths or distortion of the substrate lattice. Therefore, the calculated particle density from Cu XPS and LEIS is used to determine the mean free path of Ce 3d electrons. The best-fit mean free path shown in Figure 5.4 was found to be 0.9 nm for Ce electrons escaping through a Cu overlayer, which is slightly shorter than the literature value of 1.14 nm¹³⁶ for these 580 eV electrons through Cu.

5.3.4 Cu Film Growth Morphology on CeO_{1.95}(111) at 100 K.

The growth morphology of Cu on CeO_{1.95}(111) was investigated using He⁺ LEIS at 100 K using the same procedure as described for 300 K. The data is shown in Figure 5.5. Once again, the Cu LEIS intensity increased with Cu coverage while the Ce LEIS intensity decreased, and the data deviate strongly from the layer-by-layer (2D) growth model but are well fit by the hemispherical cap (3D) model with modified macroscopic shadowing.^{130,131} The least-squares best fit shown in Figure 5.5 gives $n = 5.3 \times 10^{13}$ particles/cm² for Cu adsorption onto CeO_{1.95}(111) at 100 K. This is ≈ 7 times greater than observed for similarly prepared CeO_{1.95}(111) surfaces and similar flux at 300 K (7.8×10^{12} particles/cm², see above). The higher density is expected at 100 K, since kinetic growth models appropriate for these conditions predict a saturation number density that varies as the inverse cube root of the Cu monomer diffusion constant across the surface,¹³⁴ which will be much smaller at 100 K than at 300 K. Within that model, this ratio of 7 corresponds to an activation energy for Cu monomer diffusion of ≈ 7 kJ/mol on CeO₂(111).

As described above, the normalized LEIS signals in Figure 5.5 directly provide the fraction of the ceria surface whose signal is masked by Cu particles. Assuming the same footprint due to macroscopic shadowing as above, these fractions can once again be divided by 1.207 to estimate the area fractions covered by Cu particles, and then divided the average Cu film thickness obtained from the Cu coverage by this covered fraction for each LEIS data point to get the average particle thickness. Figure 5.6 shows the average Cu particle thickness versus Cu coverage for both ceria films estimated in this way. These thicknesses would only decrease by 21% even assuming no macroscopic shadowing, so this hemispherical-shape assumption has only a small effect on the thickness plotted here. This thickness is again multiplied by 3 to show the corresponding average diameter along the right-hand axis. For comparison, the result expected from the same

hemispherical-cap model and particle number density as used for the best fit of Figure 5.5 shows excellent agreement. The XPS signals observed were also consistent with this hemispherical-cap model just as they were at 300 K, though these data are not presented here.

5.3.5 Heat of Adsorption and Adhesion Energy of Cu on CeO_{2-x}(111) at 300 K.

Figure 5.7 shows the heat of adsorption of Cu on CeO_{2-x}(111) (where $x = 0.05, 0.1$, and 0.2) as a function of Cu coverage at 300 K. All heats of adsorption reported here have been corrected slightly for the hot temperature and directed nature of the Cu atomic beam, so that they correspond to Cu atoms in a Boltzmann distribution at the surface temperature, and RT has been subtracted from the measured energies, as described in Chapter 2. On CeO_{1.95}(111), Cu adsorbs with an initial heat of adsorption of 300 kJ/mol and drops quickly to 283 kJ/mol by 0.1 ML. The heat then increases slowly, levelling off very near to the heat of sublimation of bulk Cu(solid), 337 kJ/mol,¹⁸ by 3.5 ML. This indicates that, at and above this coverage, incoming Cu atoms bond with the average same strength as they would to a bulk Cu surface. Increasing the degree of reduction to CeO_{1.9}(111) and CeO_{1.8}(111), decreases the initial heat of adsorption to 272 and 257 kJ/mol, respectively. There was no drop in the initial heat of adsorption with coverage for CeO_{1.90}(111) or CeO_{1.80}(111) as was observed for a small coverage range on CeO_{1.95}(111). Instead, the heats on both rose slowly to the Cu heat of sublimation by 3.5 ML. The heat of adsorption versus coverage for all three oxidation states is identical (within the scatter of the data) above 0.1 ML.

Using the Cu particle number density from the hemispherical-cap model fit to Figure 5.2 which also gives the average Cu particle diameter at each coverage, the data in Figure 5.7 can be replotted as Cu heat of adsorption vs average Cu particle diameter, as shown in Figure 5.8. The CeO_{2-x}(111) oxidation state only has an influence on the heat of adsorption for Cu nanoparticles

below 0.8 nm in diameter. Above 0.8 nm, there is no influence from the cerium oxidation state on the heat of adsorption of Cu at any coverage. Instead the heat rises to within error of the bulk Cu heat of sublimation by 2.2 nm diameter particles.

The adhesion energy of nanoparticles to the surface upon which they are grown, E_{adh} , can be calculated from the integral heat of adsorption and growth-mode data using a simple thermodynamic cycle described in Ref.⁴², and detailed in Chapter 3, which gives Equation 3.1. The adhesion energy is calculated when only <35% of the ceria surface is covered by Cu particles (according to LEIS), to ensure no significant particle agglomeration is occurring. This corresponds to a Cu coverage of 2.2 ML, or an average particle diameter of 2.2 nm. The adhesion energy for 2.2 nm diameter Cu nanoparticles supported on $\text{CeO}_{2-x}(111)$, where $x = 1.95$, was found by this equation and the data in Figure 5.7 to be 3.52 J/m^2 . This value decreased slightly for $x = 1.90$ and 1.80 to 3.45 and 3.43 J/m^2 , respectively, due to the lower adsorption energies in the first 0.1 ML on these more reduced surfaces (Figure 5.7). This adhesion energy of Cu to $\text{CeO}_{2-x}(111)$ is higher than the adhesion of 3.6 nm diameter Ag particles to the same surfaces, which was determined to be 2.3 J/m^2 . This is as expected from Ref.³¹, which shows that Cu bonds more strongly to cerium oxide surfaces than Ag. Cu adhesion to $\text{CeO}_{2-x}(111)$ is also stronger than Cu's adhesion to $\text{MgO}(100)$, which was determined to be 1.9 J/m^2 ,⁷⁴ consistent with the trend previously reported of ceria bonding Ag more strongly than $\text{MgO}(100)$.³⁹

5.3.6 Heat of Adsorption and Adhesion Energy of Cu on $\text{CeO}_{1.95}(111)$ at 100 K.

Figure 5.9 shows the heat of adsorption of Cu on $\text{CeO}_{1.95}(111)$ (where $x = 0.05, 0.1$, and 0.2) as a function of Cu coverage at 100 K compared to this same data at 300 K (reproduced from Figure 5.7). These data have again been corrected slightly for the hot temperature and directed nature of the Cu atomic beam as described above. At 100 K, Cu adsorbs with an initial heat of

adsorption of 225 kJ/mol, remains nearly constant for the first two gas pulses, and then increases with coverage to asymptotically approach the standard heat of sublimation of bulk Cu(solid) (337 kJ/mol at 300 K¹⁸ and 332 kJ/mol at 100 K¹⁸) by 5 ML. The initial heat of adsorption of Cu on CeO_{1.95}(111) at 100 K is 75 kJ/mol lower than at 300 K and remains lower at all coverages. The Cu heat of adsorption on CeO_{1.95}(111) at 100 K converges to the heat of sublimation by 5 ML, which is slower than at 300 K. The difference in initial heats of adsorption is partially due to the smaller particles at 100 K (see below), but it is also partially due to Cu nanoparticles that are aggregating primarily at step sites at 300 K while they primarily aggregate on terraces at 100 K due to slower Cu adatom diffusion (see below).

Using the particle density from the hemispherical-cap model in Figure 5.5 and the total Cu coverage in Figure 5.9, the measured heats are replotted as Cu heat of adsorption vs. average Cu particle diameter in Figure 5.10. Again the Cu heat of adsorption on CeO_{1.95}(111) at 300 K is shown for comparison. The plot is truncated for nanoparticles larger than 0.85 nm at 100 K (equivalent to 1 ML total coverage) because the fractional surface covered reached 35%, above which the hemispherical-cap model might begin to break down due to particles possibly overlapping each other. The heat of adsorption for Cu nanoparticles with a similar particle diameter in the range 0.45 to 0.8 nm is lower at 100 K than 300 K due to different adsorption sites at the two temperatures (see below). The particle density determined from the fit to the hemispherical-cap model is larger than the number of Cu atoms per unit area adsorbed in the first two gas pulses, indicating that these two calorimetry pulses produce only isolated Cu adatoms at 100 K. The effective hemispherical Cu particle diameter is 0.22 nm and 0.32 nm for these pulses, which correspond to particle volumes of 2.9×10^{-3} and 8.6×10^{-3} nm³, respectively, both smaller than the volume per atom in bulk Cu(solid), 1.18×10^{-2} nm³ based on its density.¹⁸ This is of course

impossible, which is attributed here to a breakdown of the assumption of fixed density of nuclei at such low coverages. The nuclei here are single, isolated Cu adatoms, and their number density increases in these first two pulses. These two pulses gave the same heat of adsorption within 3 kJ/mol, which does not increase with coverage (effective diameter) in this ultra-small size range as at larger sizes. This is again consistent with these two pulses producing the same structure: isolated Cu adatoms on CeO₂(111) terraces. These heats for isolated Cu adatoms average 224 kJ/mol. This value will allow for much more direct comparisons to DFT results than all our earlier calorimetry measurements of such systems, where multi-atom clusters of unknown geometry were made in the first gas pulse. Figure 5.10 represents the first measurement of the heat of any metal adsorption on any oxide which covers the full size range from isolated metal adatoms to such large metal nanoparticles that they have reached the bulk limit.

Since Figure 5.10 presents *differential* heats of adsorption, these differences in heats of adsorption with size directly reflect differences with size in the chemical potential of the metal atoms, but with opposite sign. Neglecting entropic contributions to the free energy, which change very little with particles size compared to the huge enthalpic changes here, the chemical potential of a metal atom in a particle of diameter D , $\mu(D)$, is higher than that in the bulk metal, $\mu(\infty)$, by an amount equal to the heat of sublimation of bulk Cu minus the differential heat of Cu adsorption at diameter D .⁵⁶ Thus, another way to view the data from Figure 5.10 is to plot this chemical potential (relative to that for the bulk metal, $\mu(\infty)$, which is set as the reference zero here) versus average effective diameter, as shown in Figure 5.11. Here, the first two data points at 100 K are corrected to reflect the proper effective hemisphere diameter of single, isolated atoms. As seen, these Cu adatoms at terrace sites are ≈ 110 kJ/mol higher in chemical potential than Cu atoms in particles that have reached the large-size limit (>2.5 nm). This shows why it is challenging to make so-

called single-site catalysts (i.e., isolated late transition metal adatoms on supports). This drop in chemical potential with size reflects the thermodynamic driving force for catalysts to sinter into larger particles with time on stream.^{39,56} It also reflects a decreasing propensity to bind strongly to small adsorbates, mainly associated with the decreasing degree of coordinative unsaturation as size grows.⁵⁶ Also clear in Figure 5.11 is the large decrease in chemical potential of ≈ 57 kJ/mol between Cu in dimers at step edges compared to dimers on terraces. Once the particles exceed 0.85 nm in diameter, this stabilization by step edges has diminished to an undetectable level.

5.3.7 Oxidation State of Cu and Ce During Cu Deposition Onto CeO_{2-x}(111) at 300 K

The change in oxidation state of CeO_{1.95}(111) and CeO_{1.8}(111) films as a function of Cu coverage was monitored using XPS of the Ce 3d XPS regions at 300 K. The corresponding changes in the Cu 2p XPS and Cu X-ray-excited AES peaks at a detection angle of 45° were also monitored to determine the charge state of Cu. For the Ce 3d region the same ten-peak fit described in Figure 5.1 was used to calculate the Ce³⁺ concentration at various Cu coverages, as displayed in Figure 5.12. The 4 nm thick films that were initially CeO_{1.95}(111) and CeO_{1.8}(111) become more reduced upon Cu deposition, with CeO_{1.95}(111) having a greater extent of reduction per unit of Cu coverage than CeO_{1.8}(111). The surfaces continue to reduce until 4 ML of Cu has been deposited. No further reduction was observed as thicker Cu overlayers were deposited, but no data points were taken between 4 ML and a very thick overlayer (≈ 20 ML of Cu). Szabová et al.²²⁸ similarly observed using XPS and resonant photoelectron spectroscopy (RPES) that fully oxidized CeO₂(111) was reduced with increasing Cu coverage, and found that partially reduced ceria was initially oxidized for tiny Cu coverages but then became slightly more reduced as more Cu is added. Their results are added, which cover very low coverages in much more detail, to Figure 5.12.

In the Cu 2p XPS region, no Cu²⁺-like shoulders or satellite peaks at higher binding energies on either of the 2p doublets were observed at any Cu coverage, indicating that no Cu²⁺ was present within the detection limits of the analyzer at all Cu coverages, consistent with the results of Szabová et al.²²⁸ The Cu 2p_{3/2} binding energy (BE) decreased slightly with Cu coverage up to 4 ML Cu, and stayed pretty constant after that, with a high-coverage (large-particle) saturation value of 932.67 eV. This agrees with literature values for bulk Cu(solid).²⁴⁴ At only $\approx$ 1.2 ML coverage, where the Cu particles are 1.8 nm in diameter, the Cu 2p_{3/2} BE was higher than this bulk value by only 0.25 eV on CeO_{1.95}(111) and 0.15 eV on CeO_{1.8}(111). Since the Cu and Cu⁺ spectra have a similar lineshape and binding energy in the 2p region, the Auger parameter is often used instead to differentiate neutral Cu from Cu⁺.²⁴⁵ The Auger parameter for Cu is defined as the sum of the binding energy of the Cu 2p_{3/2} peak and the kinetic energy of the Cu (LMM) AES peak. Literature values for Cu⁺ from Ref. ²⁴⁴ and Cu⁰ (as bulk Cu(solid)) are 1849.4 and 1851.3 eV, respectively. The Auger parameter for Cu increases from 1850.6 eV for 1.2 ML Cu (1.8 nm diameter) to 1851.3 eV for 4.0 ML Cu (2.7 nm diameter) on CeO_{1.95}(111) and from 1850.2 for 1.2 ML Cu (1.8 nm diameter) to 1851.3 eV for 3.7 ML Cu (2.6 nm diameter) on CeO_{1.80}(111). After $\approx$ 4 ML, the Auger parameter stays constant at 1851.3 eV up to 20 ML Cu coverage for both initial ceria oxidation states.

5.4 DISCUSSION

5.4.1 The Effect of Oxygen Vacancies at 300 K

Late transition metals usually nucleate particles at step edges when vapor deposited on oxides that are used for catalyst supports.⁵⁵ To our knowledge there are no microscopy images available for Cu on CeO_{2-x}(111). However, Cu particles were observed to nucleate at steps on

TiO₂(110),²⁴⁶ and Al₂O₃(110).²⁴⁷ Both Ag and Au have been observed to nucleate particles mainly on step edges during vapor deposition onto CeO_{2-x}(111), for x in the range from 1.91 to 2 for Ag,²⁴⁸ and from “partially reduced” to x = 2 for Au.¹⁰² It is therefore proposed here that the Cu particles here nucleate mainly at step edges for all three extents of reduction at 300 K. Since the oxygen vacancies reside mainly at step edges, and since our surfaces have ≈5 % step sites,⁷⁰ the step edges on the CeO_{1.80} surface are probably missing almost all of their oxygen atoms, whereas the steps on CeO_{1.95} have about half their oxygens still present (i.e., half stoichiometric step sites). Below it is shown that stoichiometric sites bind Cu more strongly than vacancy sites. Nevertheless, this preference for step edges over terraces is probably true even on the fully reduced step edges of CeO_{1.8}, since the saturation particle density is the same as for CeO_{1.95}. It originates as usual from the strong binding of metal adatoms to the coordinatively less saturated substrate atoms at the step edges, both O and Ce (but more strongly to O than Ce, see below).

The 42 kJ/mol decrease in the initial Cu heat of adsorption with the extent of reduction of CeO_{2-x}(111) (Figure 5.7) is opposite to the previous observation for Ag adsorption on CeO_{2-x}(111), where Ag initially binds 25 kJ/mol more strongly to CeO_{1.9}(111) than to CeO_{1.8}(111).⁷⁰ This suggests that Cu binds more strongly to stoichiometric ceria sites than to oxygen vacancies, whereas Ag binds to oxygen vacancies more strongly than to stoichiometric sites. This marked contrast between Cu and Ag is qualitatively consistent with DFT results. Szabová et al.¹⁵⁰ and Yang et al.¹⁵¹ predicted with DFT that Cu binds more strongly to stoichiometric sites than to oxygen vacancies on CeO₂(111) terraces, by 1.4 eV and 1.2 eV (135 kJ/mol and 116 kJ/mol), respectively; whereas Luches et al.²⁴⁹ predicted with DFT that Ag binds more weakly to stoichiometric sites than to oxygen vacancies on CeO₂(111) terraces. Similarly, DFT indicates

that Au,^{109,116,145} Pt²⁵⁰ and Pd⁴⁴ bind more weakly to stoichiometric sites than to oxygen vacancies on CeO₂(111) terraces (this was confirmed in Chapter 3 for Au).

Our measured initial heats of Cu adsorption onto CeO_{2-x}(111) have a much smaller decrease between CeO_{1.95}(111) and CeO_{1.8}(111) (42 kJ/mol) than the ≈ 1.3 eV (≈ 125 kJ/mol) difference between vacancy sites and stoichiometric sites on terraces predicted by DFT highlighted above. However, one does not expect the full difference in adsorption energy for monomers to be seen in those measurements, since the 0.44 nm diameter Cu particles that are made in the first data point will prefer to avoid oxygen vacancy sites to the extent possible. It is proposed that these Cu particles are located at step edges, which is also where the oxygen vacancies mainly reside, so it is not entirely possible to avoid oxygen vacancies on the two more reduced surfaces. Differences compared to the DFT adsorption energies are also expected due to the strong role of steps here, which were not considered in those DFT calculations.

The nucleation of Cu clusters occurs on stoichiometric step sites first, followed by the Cu particles spreading onto less favorable sites (terraces and step vacancies) as they grow in diameter. This is the reason for the initial decrease in heat of Cu adsorption with coverage on the least reduced surface. The resulting decrease in binding energy of Cu atoms to the support apparently exceeds the usual increase in binding energy due to the formation of more Cu-Cu bonds per adatom as the size grows. At ≈ 0.1 ML (0.8 nm diameter), the latter effect starts to dominate, and so the heat increases with further Cu adsorption. Such stoichiometric step sites are not available on the two more reduced surfaces in sufficient quantity to see the high initial heat of adsorption due to nuclei mainly on such sites, and so the minimum in heat versus coverage is also not seen. Isolated oxygen vacancies on terraces are also potential nucleation sites for metal nucleation. However,

since DFT predicts that the heat of adsorption of Cu atoms is much weaker on oxygen vacancies on CeO₂(111) terraces compared to stoichiometric terrace sites,^{150,151} this is certainly not expected.

The saturation Cu particle density remained constant when the degree of CeO_{2-x}(111) reduction was increased from $x = 0.05$ to $x = 0.2$. This is consistent with the step density being the same on these surfaces (as expected²⁴²), with particle nucleation only occurring at step edges (including their kink sites). It is somewhat surprising that the density of particles per unit step length remains the same. This may be due to particle-particle repulsion along step edges. Such repulsion is apparent in STM images of Ag and Au particles on CeO₂(111), where the particle-particle separations along step edges are far more uniform than expected for randomly-located particles.^{102,248} Such repulsion could result from the adsorbed particles inducing strain in the ceria lattice or having dipole moments perpendicular to the surface.

According to DFT, Cu adsorption to oxygen vacancies on CeO₂(111) terraces causes transfer of electron density from Ce³⁺ to Cu, forming a partial negative charge on Cu and the oxidation of Ce³⁺ toward Ce⁴⁺, whereas Cu on stoichiometric terrace sites does the opposite, transferring electron density from Cu to Ce⁴⁺, reducing it toward Ce³⁺.^{150,151} At 1.2 ML in Figure 5.12, the Cu particles cover $\approx 20\%$ of the surface (Figure 5.2a). At this fractional coverage by Cu particles, they must bind both to step edges (which cover $\approx 5\%$ of the surface and are dominated by oxygen vacancies) and to stoichiometric terrace sites, with possibly some binding to terrace vacancies as well. Thus, according to DFT, the ceria oxidation state shift in Figure 5.12 should be a competition between two opposing effects, ceria oxidation by Cu at oxygen vacancies and Ce reduction by Cu at stoichiometric sites. The competing interactions explain the smaller overall reduction of ceria observed for CeO_{1.80} compared to CeO_{1.95} where fewer oxygen vacancies are available initially (Figure 5.12).

To quantify the extent of charge transfer per Cu atom in Figure 5.12, it can be assumed that the Ce XPS signal probes a depth of ≈ 1.0 nm (see above), which corresponds to 2.5×10^{15} Ce atoms per cm^2 being probed at the bulk density of CeO_2 (2.52×10^{22} Ce atoms cm^{-3}). The slope of the lines here corresponds to the number of electrons gained per Ce atom in this probe depth per Cu ML, where 1 ML is 7.9×10^{14} Cu atoms per cm^2 . These slopes thus correspond to 0.17 and 0.13 electrons donated per Cu atom for 1.2 ML and 4 ML Cu, respectively, on $\text{CeO}_{1.95}(111)$, and 0.060 and 0.053 electrons donated per Cu atom for 1.2 ML and 3.7 ML Cu, respectively, on $\text{CeO}_{1.80}(111)$. This apparent extent of charge transfer per Cu atom is less than half as much on $\text{CeO}_{1.80}$ compared to $\text{CeO}_{1.95}$, due to this competition between Ce reduction by Cu at stoichiometric sites and ceria oxidation by Cu at oxygen vacancies.

The apparent reduction of $\text{CeO}_{2-x}(111)$ in Figure 5.12 may be partly because Cu adsorbs primarily to the stronger-binding stoichiometric sites compared to vacancy sites, which would preferentially attenuate the Ce^{4+} XPS signal, causing an apparent decrease in Ce oxidation state. The mobility of surface oxygens in the top layer may even be sufficient to allow them to move under the Cu particles and displace vacancies toward the uncovered parts of the surface. This selective Ce^{4+} signal blocking offers an additional contribution to understanding Figure 5.12, but means that its quantitative interpretation in terms of electrons transferred per Cu atom is an overestimate. It is also consistent with the lower apparent extent of reduction of ceria on the more reduced surface, since that surface has fewer stoichiometric sites whose Ce^{4+} signal can preferentially be blocked by Cu.

The different shifts in the Cu $2p_{3/2}$ BEs and the Cu Auger parameters for Cu on $\text{CeO}_{1.80}$ compared to $\text{CeO}_{1.95}$ are also consistent with a competition between Ce reduction by Cu at stoichiometric sites and ceria oxidation by Cu at oxygen vacancies, with more of the latter

occurring on $\text{CeO}_{1.80}$. To better understand these shifts, they must be analyzed in some detail. Qualitatively similar shifts in the Cu $2p_{3/2}$ BE and Auger parameter to those observed here were seen by Madey et al.²⁴⁵ for Cu nanoparticles on a thin film of $\text{Al}_2\text{O}_3(0001)$ on $\text{Re}(0001)$, who analyzed them in quantitative detail to determine the initial- and final-state contributions to the Cu BE shift. That same method was used to analyze Ag nanoparticles on slightly reduced $\text{CeO}_2(111)$.¹³⁹ This same method is now applied to analyze the present data at 1.2 ML Cu, where the average particle diameter is 1.8 nm. Compared to the high-coverage (bulk Cu) limit, the Cu $2p_{3/2}$ BE at this coverage on $\text{CeO}_{1.95}(111)$ was 0.25 eV higher ($\Delta\text{BE} = +0.25$ eV) and the Cu Auger parameter was 0.7 eV smaller ($\Delta\alpha = -0.7$ eV). Dividing $\Delta\alpha$ by -2 gives an estimate of the BE shift due to final-state relaxation effects, which here is $-\Delta\alpha/2 = +0.35$ eV. Subtracting this from the observed BE shift of +0.25 eV gives an estimate of the initial-state BE shift alone, which is $(0.25 - 0.35)$ eV = -0.1 eV. At this coverage on $\text{CeO}_{1.80}(111)$, $\Delta\text{BE} = +0.15$ eV and $\Delta\alpha = -1.1$ eV. Dividing $\Delta\alpha$ by -2 gives an estimate of the BE shift due to final-state relaxation effects, which here is $\Delta\alpha/2 = +0.55$ eV. Subtracting this from the observed BE shift of +0.15 eV gives an estimate of the initial-state BE shift alone, which is $(0.15 - 0.55)$ eV = -0.4 eV. This decrease in Cu $2p_{3/2}$ BE (after correction for final-state effects) for 1.8 nm particles on both surfaces (relative to bulk Cu) suggests some transfer of electron density from the ceria to the Cu, which is perhaps insignificantly small on $\text{CeO}_{1.95}(111)$, but quite significant on $\text{CeO}_{1.80}(111)$. The transfer of a slight amount of electron density from Cu to ceria, apparent from Figure 5.12, is not detected through this analysis of Cu peak positions. This may be associated with a failure of the assumption, implicit in this analysis that the change in Auger parameter is only due to final-state effects, when initial-state effects could also contribute to $\Delta\alpha$.

These results are consistent with DFT calculations which predict that Cu adsorption to oxygen vacancies on CeO₂(111) causes transfer of electron density from Ce³⁺ to Cu, forming a partial negative charge on Cu.^{150,151} There are more vacancies where this can occur on the more reduced CeO_{1.8}(111) surface. On the CeO_{1.95}(111), this still occurs at step edges only, but the opposite effect occurs to a greater extent at the stoichiometric sites on both steps and terraces. No broadening in the Cu 2p_{3/2} peak was observed compared to the highest Cu coverage, as might be expected when both effects occur, but not surprising since they occur at the base of the same Cu particle, whose delocalized electrons bring it to a single average potential.

This interpretation is consistent with the results of Szabová and Matolin et al.²²⁸ shown in Figure 5.12, whereby Cu reduced stoichiometric CeO₂(111), but initially oxidized the heavily reduced CeO_{1.73}(111) surface. Because Cu adsorbs mainly at step edges at very low coverage on CeO_{1.73}(111), Cu is mainly binding to oxygen vacancies, where DFT predicts that it will gain electron density from ceria.^{150,151}

While it is energetically very unfavorable to reduce Al³⁺ with Cu to form Cu⁺,^{42,245} and no reduction of Al₂O₃ was observed upon Cu adsorption,¹³⁰ ceria is much easier to reduce. Nevertheless, the net reaction $2 \text{CeO}_2(\text{solid}) + 2 \text{Cu}(\text{s}) \rightarrow \text{Ce}_2\text{O}_3(\text{solid}) + \text{Cu}_2\text{O}(\text{solid})$ is still uphill by 212 kJ/mol (calculated from their standard heats of formation). Experimental trends in metal reduction of oxides upon adsorption at submonolayer coverages and 300 K closely follow bulk thermodynamic predictions as described by Campbell.⁴² According to that trend, this +212 kJ/mol is sufficiently endothermic that one would not expect Cu to reduce ceria. This lends further support to the explanation for the apparent reduction of ceria in Figure 5.12 as arising from selective attenuation of the Ce⁴⁺ XPS signal by Cu, due to its preference for stoichiometric sites. The reaction enthalpy remains almost as endothermic (less by only ≈ 50 kJ/mol O) when one considers

the analogous bulk reaction but where $\text{Ce}_2\text{O}_3(\text{solid})$ is replaced by $\text{CeO}_{1.99}$, i.e., representing a very slight reduction.²⁵¹ At some point near that stoichiometry, entropic effects will tip the bulk thermodynamic balance.

5.4.2 Binding of Isolated Cu Atoms at 100 K and the Chemical Potential of Clusters

In Figure 5.10, the difference in the heats of adsorption at 100 K versus 300 K for Cu on $\text{CeO}_{1.95}(111)$ for nanoparticles of the same size below 0.85 nm in diameter is attributed to differences in binding sites of the nanoparticles. Although there are no STM images available for Cu adsorption on $\text{CeO}_{1.95}(111)$, it was proposed in the previous section that the majority of Cu atoms deposited at 300 K are nucleated into nanoparticles at step edges (including kink sites) to explain adsorption heats and other data at 300 K for Cu on $\text{CeO}_{1.95}(111)$, most importantly the initial decrease in heat of adsorption with coverage and particle size (Figure 5.9 and Figure 5.10) as these step sites get titrated. This is consistent with STM results for similar systems (nanoparticles of Ag^{248} and Au^{102} on $\text{CeO}_2(111)$ and Cu on $\text{Al}_2\text{O}_3^{247}$ and $\text{TiO}_2(110)^{246}$ at 300 K).

When cooling to 100 K, the particle density increases 7-fold compared to 300 K (5.3×10^{13} vs. 7.8×10^{12} particles/cm², respectively). Similar increases in particle density were observed in Chapter 3 for Au on $\text{CeO}_2(111)$ at 100 versus 300 K, as well as by Lu et al.¹⁰² and Baron et al.¹⁰⁷, with the increased density at 100 K due to Au particles nucleated on terraces as opposed to much more predominantly at steps at 300 K. The increased particle density for Cu/ $\text{CeO}_{1.95}(111)$ at 100 K is also attributed to nucleation of Cu nanoparticles mainly on terraces, whereas they nucleate mainly on steps at 300 K.¹²⁶ This explains the 52 kJ/mol lower heat of adsorption at 100 K versus 300 K in Figure 5.9 for 0.44 nm diameter Cu particles (the smallest Cu nanoparticles measured at 300 K), given the well-known lower stability metal nanoparticles on terraces compared to steps.²⁵² This difference in heats of adsorption slowly diminishes with size to zero by 0.85 nm, probably

because the increasing footprint of the Cu particles is mainly associated with their expanding onto terraces above 0.85 nm, even when they started at step edges. The nanoparticles are probably not exclusively nucleated at steps for adsorption at 300 K nor terraces at 100 K, but these are their dominant nucleation sites.

Since this surface has 2.5% oxygen vacancies (mainly at step edges, see above) the Cu atoms may be located at a mixture of oxygen vacancies and stoichiometric ceria sites. However, since DFT results from both Szabová et al.¹⁵⁰, and Yang et al.¹⁵¹ predicted that Cu binds 1.4 eV to 1.2 eV (135 kJ/mol and 116 kJ/mol) more strongly to stoichiometric ceria sites on (111) terraces than to oxygen vacancies in (111) terraces, consistent with our experimental result that Cu in 0.4 nm diameter particles is >40 kJ/mol less stable on the more reduced CeO_{1.8}(111) surface than on CeO_{1.95}(111) (see above), the isolated Cu adatoms produced here at 100 K on terraces surely adsorb only to stoichiometric sites, and avoid bonding to oxygen vacancies (which are located at step edges anyway). At 300 K, Cu diffuses fast enough to reach step edges, where it binds more strongly than at terraces in spite of these steps missing about half their oxygens.¹²⁶

These results provide benchmarks to test the energy accuracy of computational estimates of metal bonding to oxide surfaces. Table 5.1 compares the measured adsorption energy for Cu adatoms on stoichiometric CeO₂(111) to published DFT+U results at its most stable adsorption geometry (using periodic boundary conditions within the generalized gradient approximation (GGA)). In order to properly describe the localization of the Ce 4f electrons, a Hubbard parameter (U) was added to the functionals, as summarized in Table 5.1.^{229,230,232} These calculated Cu adsorption energies are generally higher by 30 – 69 kJ/mol than our experimental result. Since the heat capacity of solids is generally smaller than gases at low temperature, part of this difference may be due to the fact that the calculation is at 0 K while the measurement is at 100 K. This could

only account for <2.1 kJ/mol of the difference since the average heat capacity difference is surely less than the heat capacity of Cu(gas) ($5/2 R$). The main difference can be associated with the use of large U values. The calculation by Marta Branda et al.³¹ using a lower U (3 eV) is the only one to underestimate the adsorption energy, although the magnitude of the error is not improved. Huang et al.²³¹ showed that calculated adsorption energies for CO on CeO₂(111) were better represented using lower U values (2-3 eV), and suggested that lower U is probably required whenever describing electron transfer reactions. Also listed in Table 5.1 are the charge transfers predicted by DFT, which are generally >+0.66. The PBE +4.5 functional gives a greater degree of charge transfer than PBE +5; however, PW91 gives a similar extent of charge transfer independent of U . Our XPS results (see above) and RPES results from Szabová et al.²²⁸ indicate that only a small amount of electron density is transferred from Cu to CeO₂(111), less than 0.17 electrons per Cu atom at 1.2 ML Cu coverage.¹²⁶ It thus seems that all these DFT functionals overestimate the extent of charge transfer, although the charge transfer per Cu atom is not known from experiments at the low coverage and temperature required to maintain isolated Cu adatoms.

5.5 CONCLUSION

Using LEIS and XPS, Cu was found to grow as 3D particles CeO_{2-x}(111) with a fixed particle density of 7.8×10^{12} particles/cm² at all extents of reduction ($x = 0.05$ up to 0.2) at 300 K. Copper atoms adsorb onto reduced CeO_{1.95}(111) at 300 K with an initial heat of adsorption of 300 kJ/mol. They adsorb initially more weakly to the more oxygen deficient CeO_{1.90}(111) and CeO_{1.8}(111) surfaces (272 and 257 kJ/mol, respectively). This is the first late transition metal studied by adsorption calorimetry on any oxide to show this stronger bonding to stoichiometric sites compared to sites with oxygen vacancies. The heat of adsorption on CeO_{1.95}(111) then decreases with coverage up to 0.1 ML, due to the Cu particles spreading from stoichiometric step

edges to step sites with vacancies and terrace sites as their size grows up to 0.8 nm diameter. Above a total Cu coverage of ≈ 0.1 ML (>0.8 nm diameter), incoming Cu atoms adsorb with the same average heat of adsorption on all three ceria oxidation states, increasing with coverage (particle size) to the bulk Cu(solid) heat of sublimation by 3.5 ML (2.2 nm diameter). Cu adsorption causes a faster decrease in the Ce^{4+} XPS signal compared to Ce^{3+} in the Ce 3d XPS region, due to its selective binding at stoichiometric sites and the transfer of a small amount of electron density from Cu to ceria (<0.17 electrons per Cu atom). The adhesion energy of 2.2 nm Cu nanoparticles onto $\text{CeO}_{1.95}(111)$ at 300 K was determined to be 3.52 J/m^2 and decreased to 3.45 and 3.43 J/m^2 for $\text{CeO}_{1.90}(111)$ and $\text{CeO}_{1.80}(111)$, respectively.

Copper atoms adsorb onto $\text{CeO}_{1.95}(111)$ at 100 K with a nearly constant heat of adsorption of 224 kJ/mol at very low coverage, associated with Cu adatoms on stoichiometric terrace sites. Above 0.05 ML, Cu grows as 3D Cu nanoparticles on $\text{CeO}_{1.95}(111)$ at 100 K, with a fixed particle density of $5.3 \times 10^{13} \text{ particles/cm}^2$, 7-fold larger than at 300 K. The heat of Cu adsorption when making Cu nanoparticles with an average diameter of 0.45 to 0.8 nm is lower at 100 K than at 300 K by ≈ 50 to 30 kJ/mol on the same $\text{CeO}_{1.95}(111)$ surface, attributed to cluster nucleation on terrace sites at 100 K instead of the more stable step edge sites at 300 K. Figure 5.11 summarizes the measured chemical potential of Cu atoms versus Cu nanoparticle size at both stoichiometric $\text{CeO}_2(111)$ terraces and step edges with $\approx 50\%$ oxygen vacancies. Since Cu is less stable near oxygen vacancies on this surface, it will avoid bonding near them upon adsorption. Thus, the results for the smallest Cu clusters are not strongly influenced by the $\approx 2.5\%$ oxygen vacancies present on $\text{CeO}_{1.95}(111)$. Therefore, the monomer and dimer energies in Figure 5.11 are considered to be representative of stoichiometric $\text{CeO}_2(111)$ sites. Comparison to DFT+U calculations shows that calculated monomer adsorption energies differ from this experiment by -44 to $+69 \text{ kJ/mol}$.

5.6 FIGURES

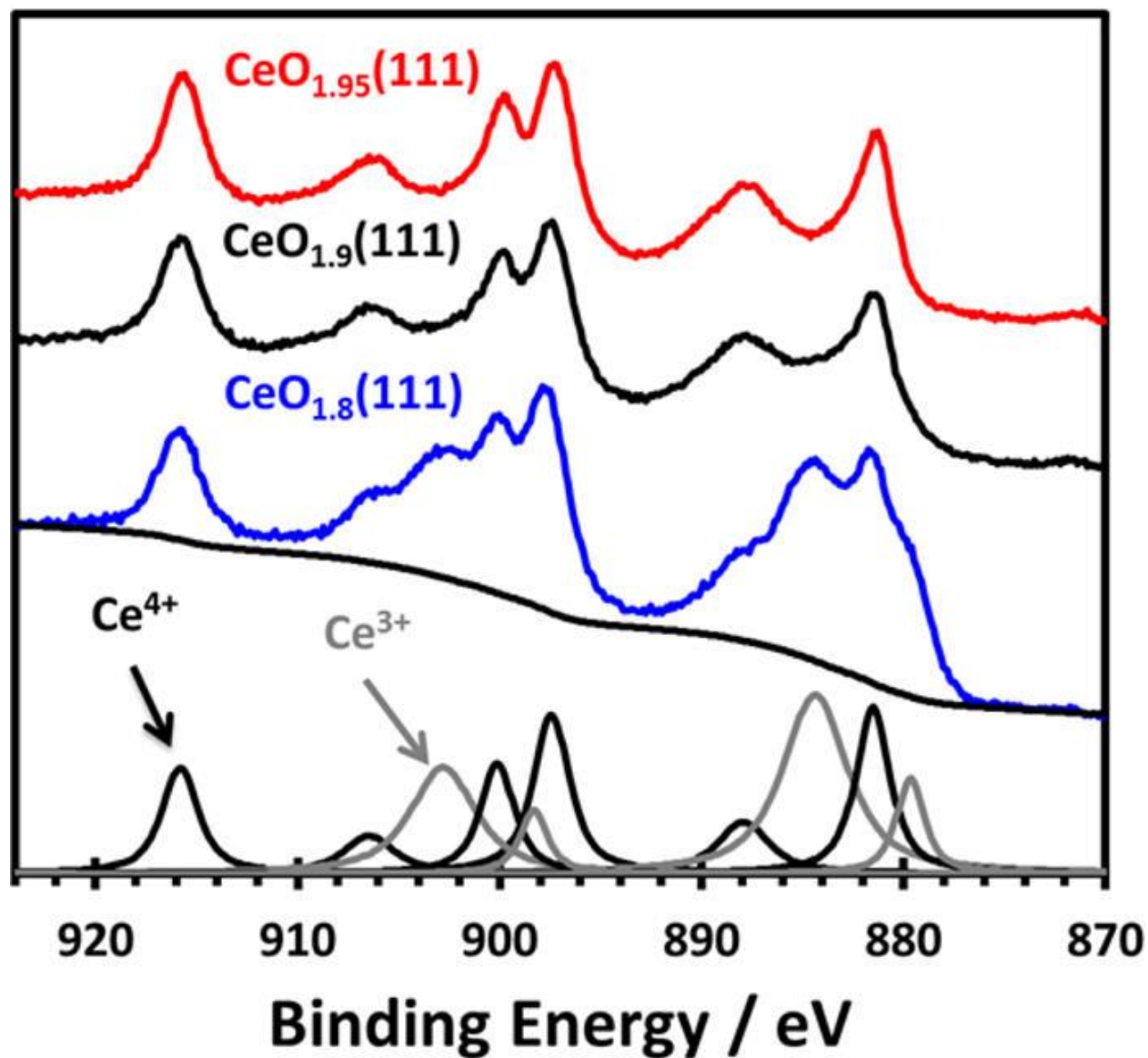


Figure 5.1. Representative Al K α XPS spectra of Ce 3d region collected at 300 K on 4 nm thick $\text{CeO}_{2-x}(111)$ films grown on Pt(111) with stoichiometries of (a) $\text{CeO}_{1.95}(111)$, (b) $\text{CeO}_{1.90}(111)$, and (c) $\text{CeO}_{1.80}(111)$ with the Shirley background subtracted for peak fitting, and (d) an example deconstruction of the Ce 3d region for $\text{CeO}_{1.80}(111)$ in spectrum (c) used for determining the cerium oxidation state. The more reduced films were prepared by growing $\text{CeO}_{2-x}(111)$ in a lower O_2 background pressure and post annealing to the desired oxidation state.

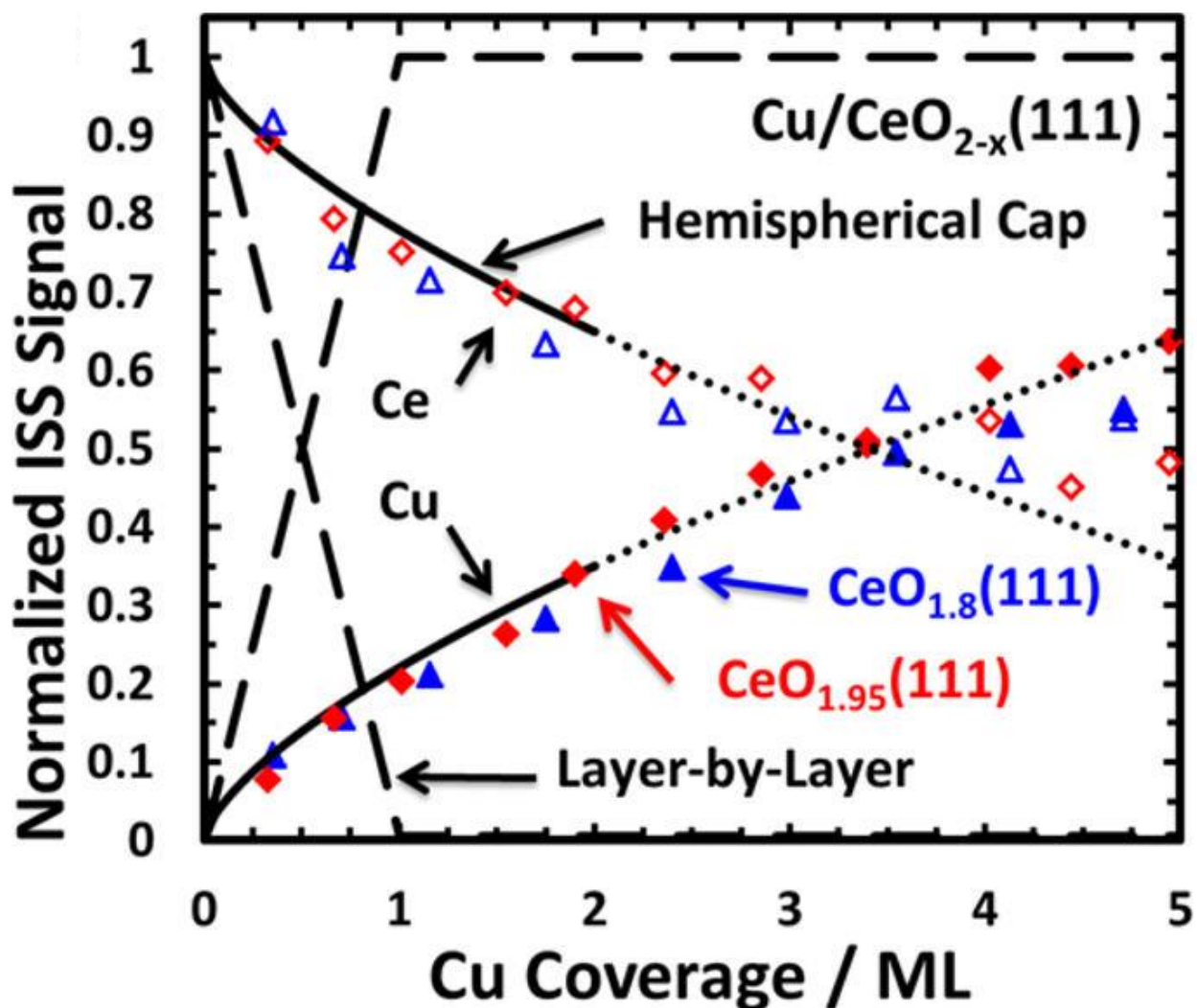


Figure 5.2. Integrated Cu (closed symbols) and Ce (open symbols) LEIS signal intensities (normalized to thick multilayer Cu and clean CeO_{2-x}(111), respectively) as a function of Cu coverage after deposition onto CeO_{1.95}(111) (diamonds) and CeO_{1.8}(111) (triangles) at 300 K. The dashed line corresponds to the normalized LEIS signal that would be observed if Cu grew in a layer-by-layer fashion, while the solid line corresponds to Cu growing as hemispherical caps with a fixed radius and a fixed particle density of 7.8×10^{12} particles/cm². This model is only reasonable up to $\approx 35\%$ of the surface being covered by particles, since they may start to overlap with each other at higher coverage, so the dotted lines after that are only a guide to the eye.

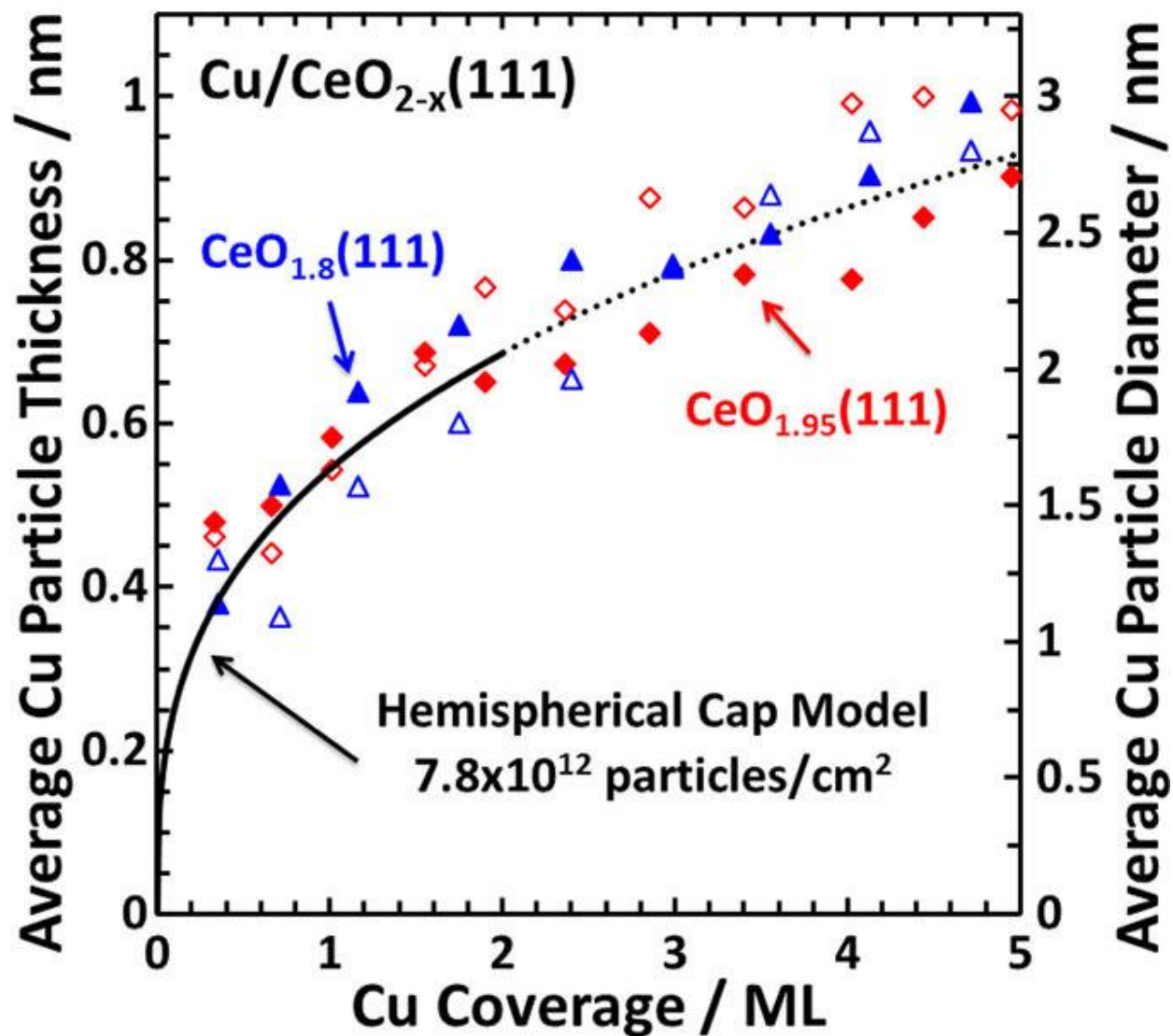


Figure 5.3. The average Cu particle thickness versus Cu coverage calculated from the Cu (closed) and Ce (open) LEIS data points of Figure 5.2, and on the right axis, the average diameter of hemispherical caps that corresponds to this thickness. Also shown is the result expected for the same hemispherical-cap model and particle number density as used for the best fit to the data in Figure 5.2.

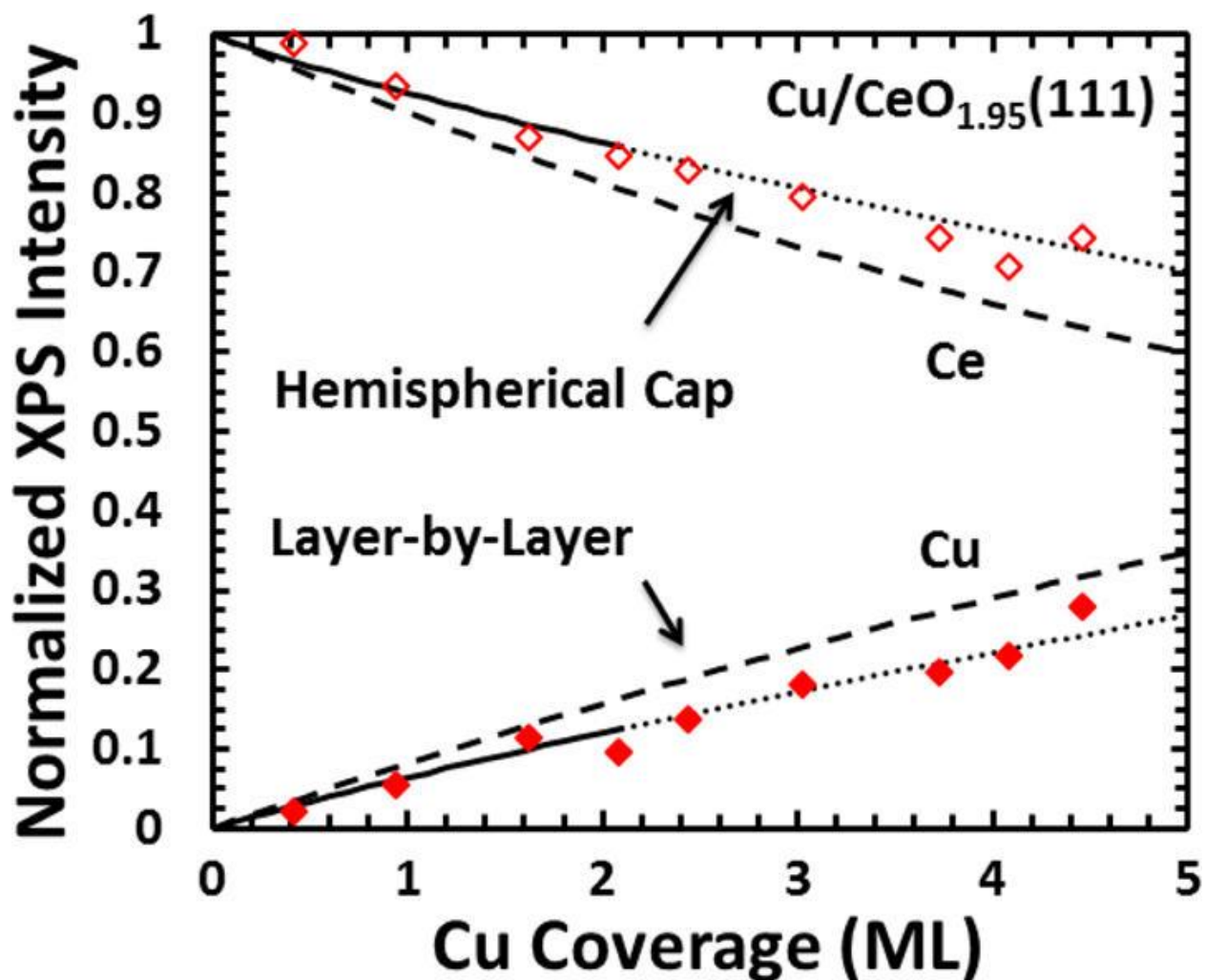


Figure 5.4. Integrated Cu 2p_{3/2} (closed) and Ce 3d (open) XPS signal intensities (detected normal to the surface) normalized to bulk Cu and clean CeO_{2-x}(111) respectively as a function of Cu deposition at 300 K onto CeO_{1.95}(111). These are the averages of three separate runs that were the same within scatter. The dashed line corresponds to the normalized XPS signal that would be observed if Cu grew in a layer-by-layer fashion, while the solid line corresponds to Cu growing as hemispherical caps with a fixed radius and a fixed particle density of 7.8×10^{12} particles/cm² (which is valid only up to ≈ 2.2 ML, see above).

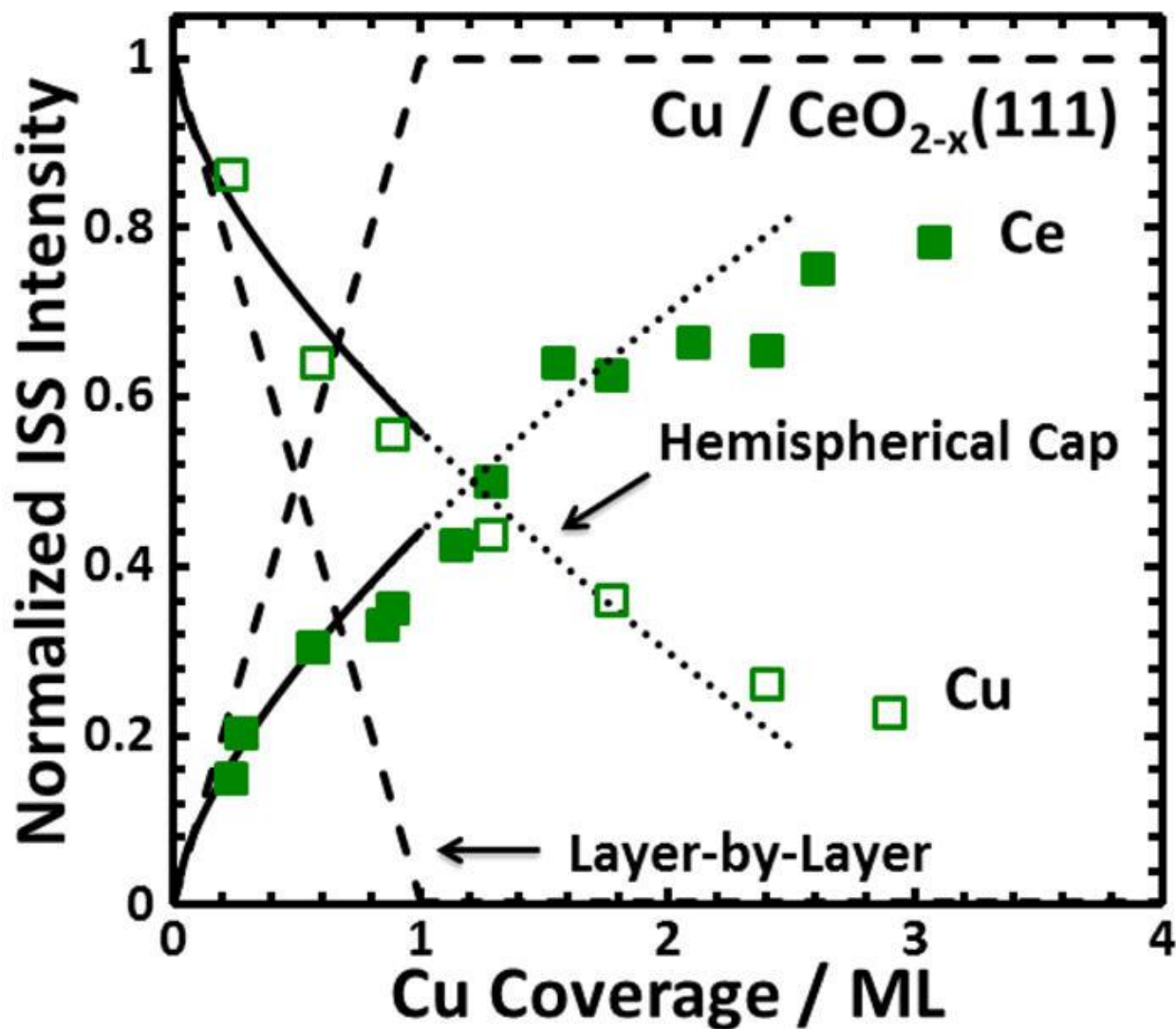


Figure 5.5. Integrated Cu (closed) and Ce (open) LEIS signal intensities normalized to bulk like (>40 ML) Cu and clean $\text{CeO}_{1.95}(111)$ respectively as a function of total Cu coverage at 100 K onto $\text{CeO}_{1.95}(111)$. The dashed line represents a layer-by-layer fit for 2-dimensional growth of Cu. The solid line represents a hemispherical cap fit with a fixed particle density of 5.3×10^{13} particles/cm².

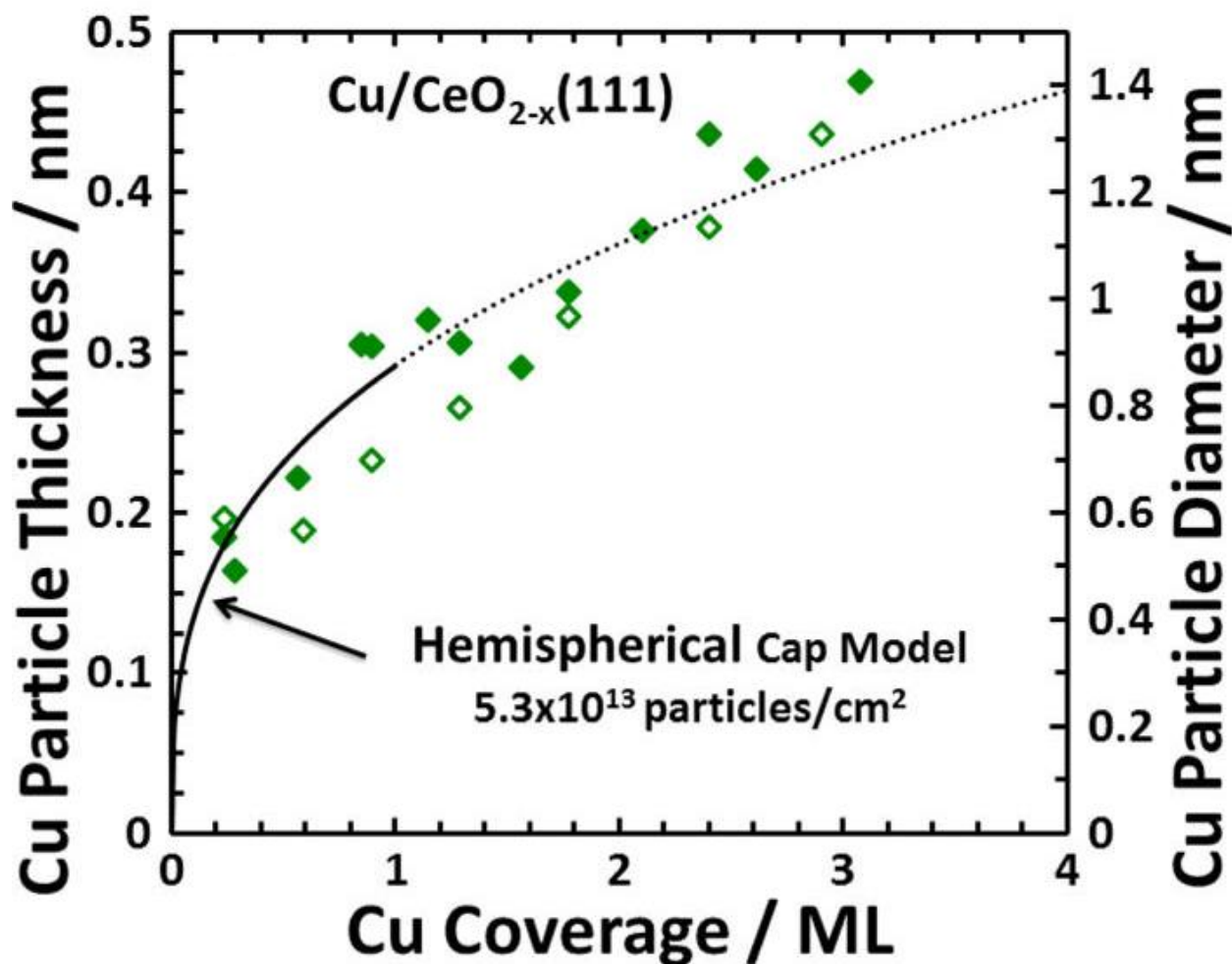


Figure 5.6. The average Cu particle thickness versus Cu coverage at 100 K calculated from these LEIS data points, and on the right axis, the average effective diameter of hemispherical caps that corresponds to this thickness. Also shown is the result expected for the same hemispherical-cap model and particle number density as used for the best fit to the data in Figure 5.5.

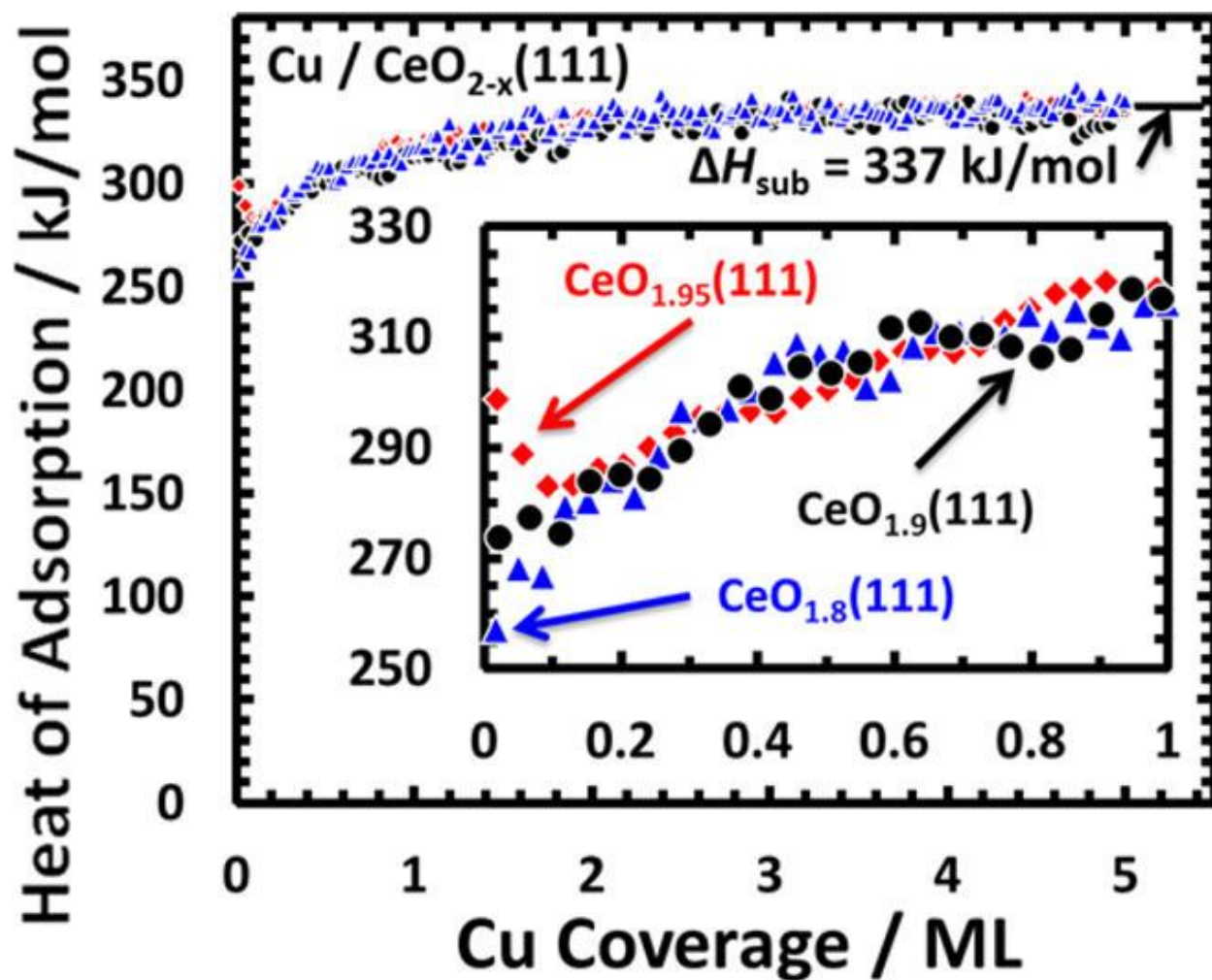


Figure 5.7. Heat of Cu atom adsorption on $\text{CeO}_{1.95}(111)$ (diamonds) [average of 5 experiments], $\text{CeO}_{1.90}(111)$ (circles) [average of 3 experiments] and $\text{CeO}_{1.8}(111)$ (triangles) [average of 3 experiments], all at 300 K, as a function of Cu coverage.

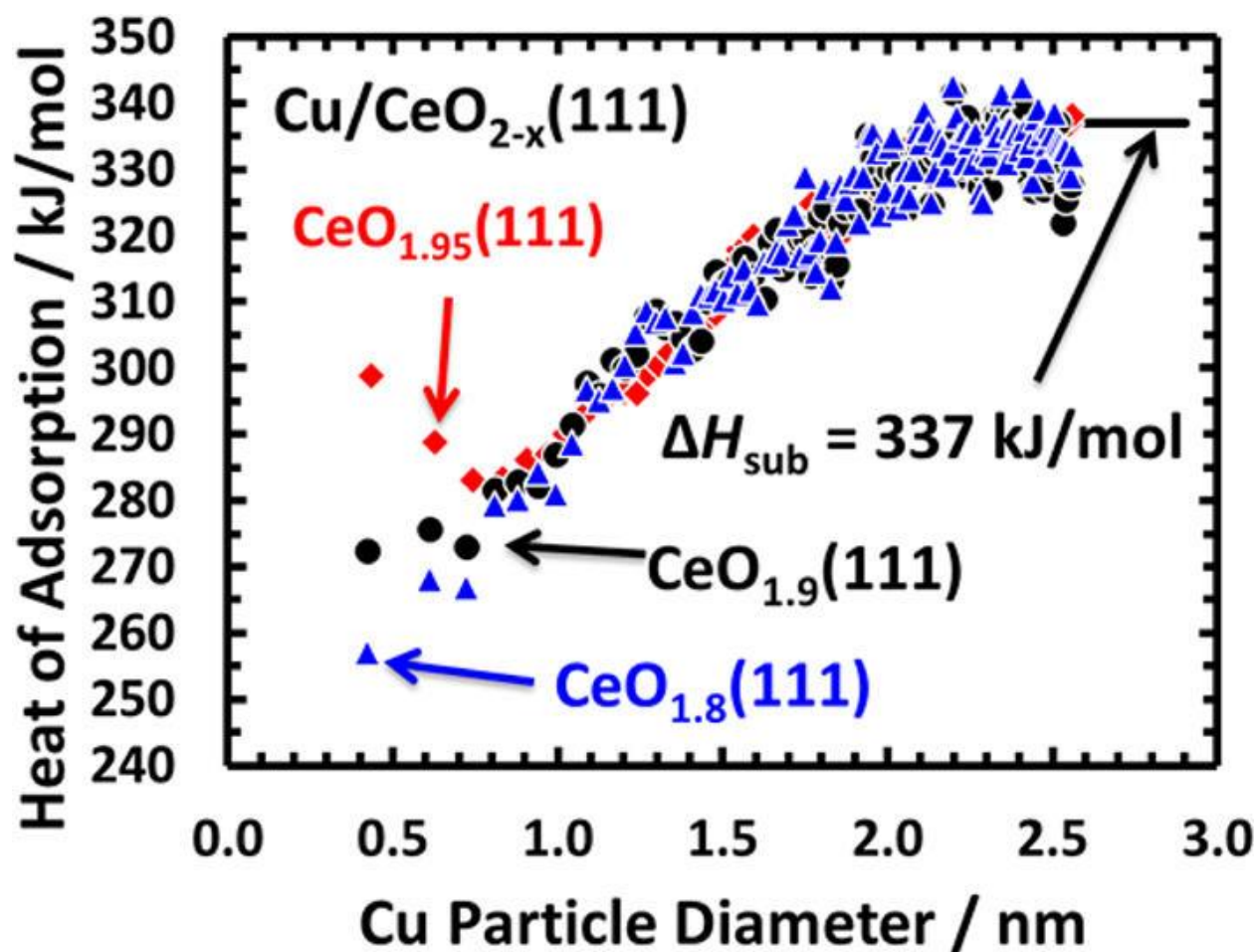


Figure 5.8. Heat of Cu atom adsorption CeO_{1.95}(111) (diamonds) [average of 5 experiments], CeO_{1.90}(111) (circles) [average of 3 experiments] and CeO_{1.80}(111) (triangles) [average of 3 experiments], all at 300 K, as a function of the average Cu particle diameter to which Cu atoms add.

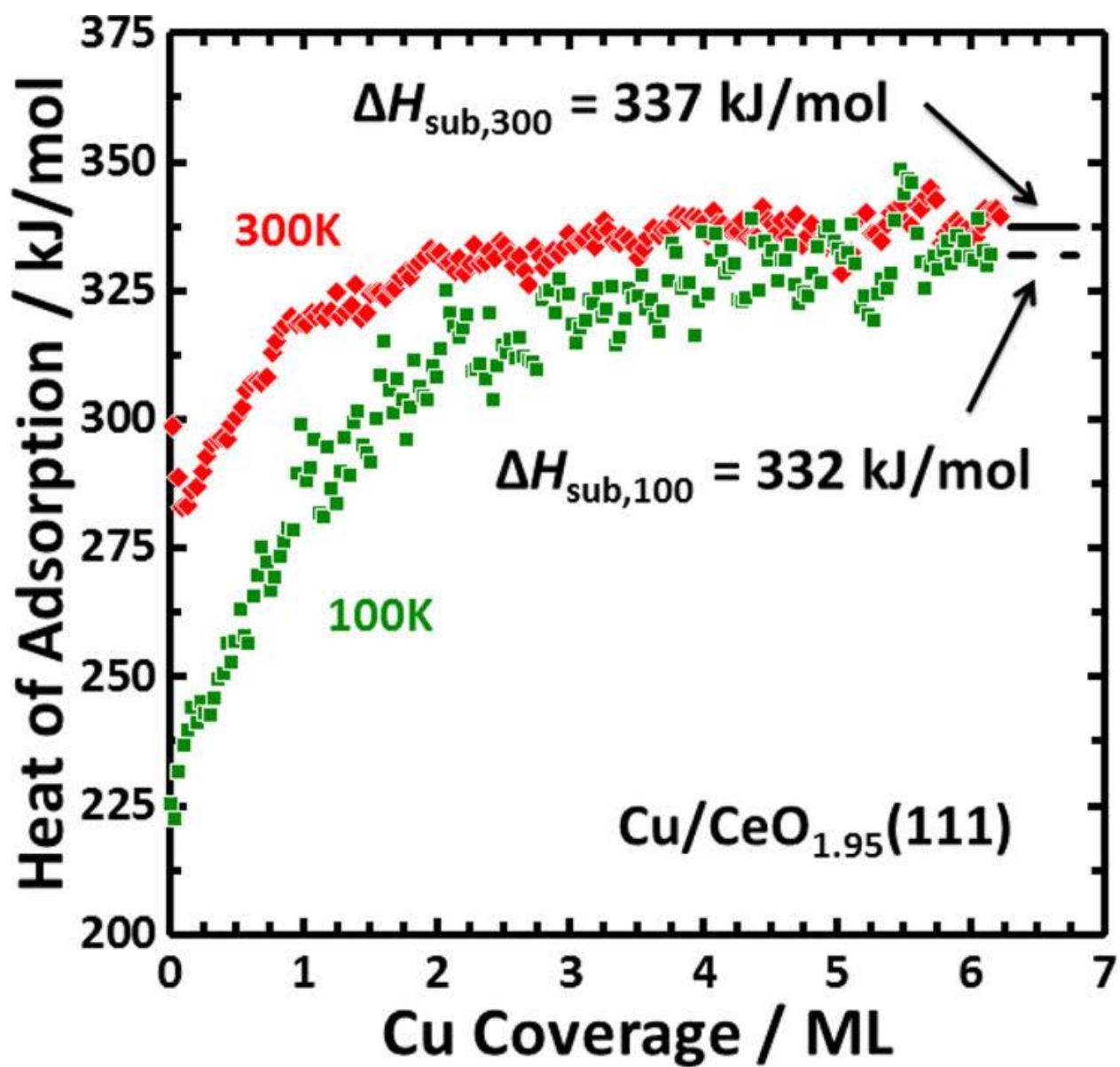


Figure 5.9. Cu atom heat of adsorption at 300 K (red diamonds) and 100 K (green squares) on $\text{CeO}_{1.95}(111)$ as a function of Cu coverage.

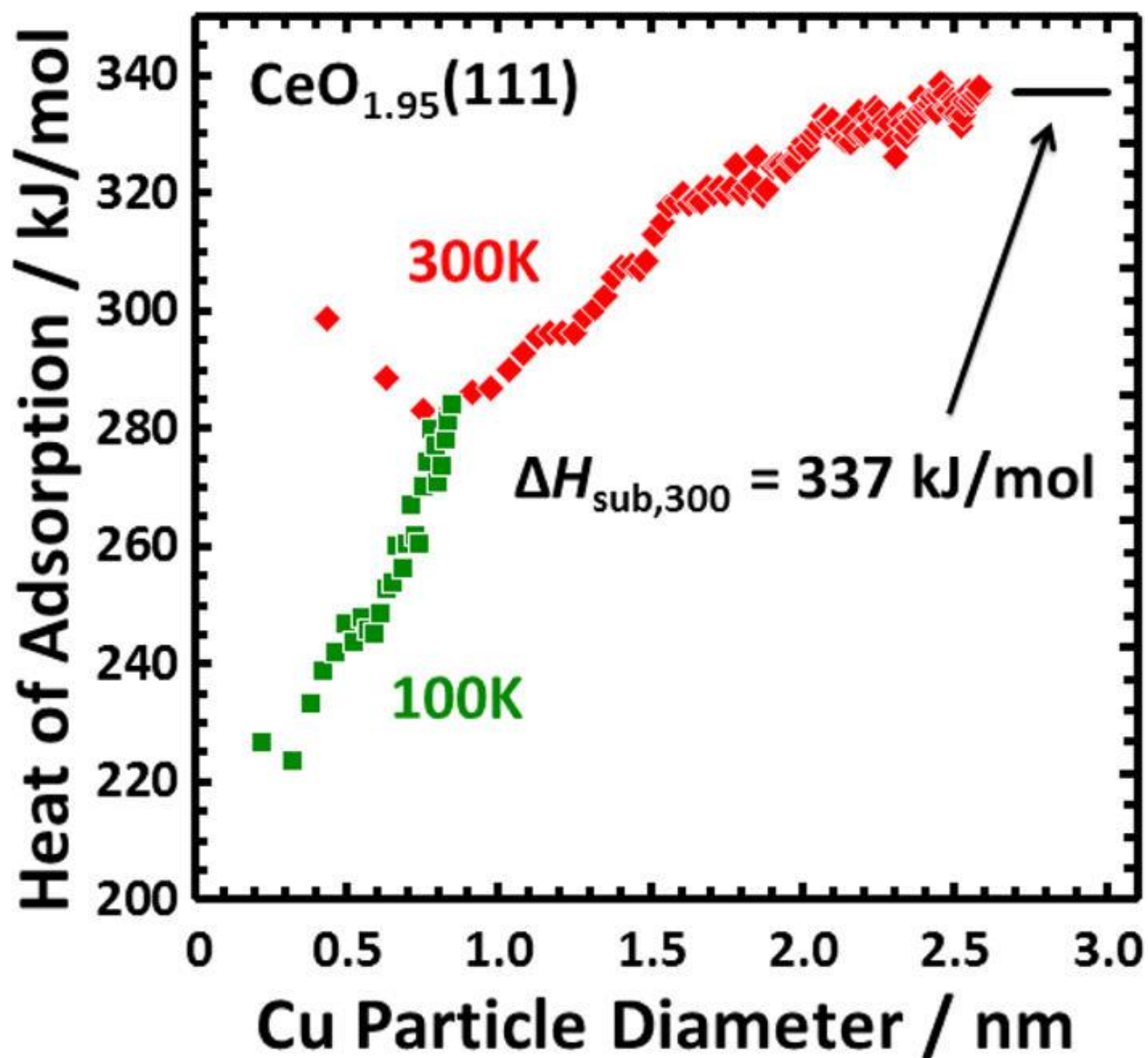


Figure 5.10. Cu atom heat of adsorption at 300 K (red diamonds) and 100 K (green squares) on CeO_{1.95}(111) as a function of average Cu particles diameter after adsorption. The effective particle diameter was calculated using the total Cu coverage, assuming the nanoparticles grow as hemispherical caps with a constant particle density of 5.3×10^{13} particles/cm². The data at 300 K and 100 K was truncated at 35% total surface coverage to avoid heats when particles were agglomerating.

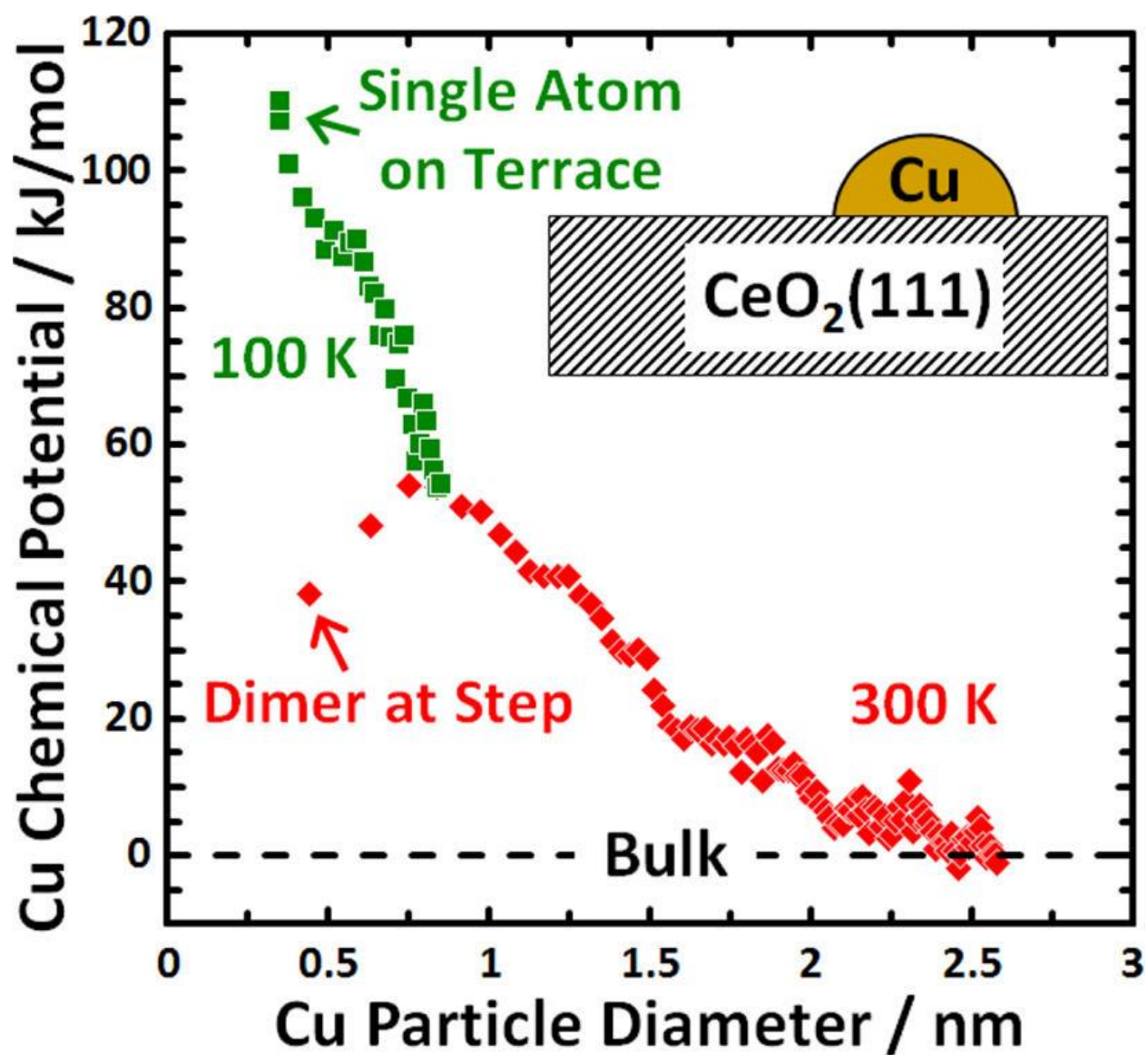


Figure 5.11. The chemical potential of Cu atoms in Cu nanoparticles on CeO_{1.95}(111), relative to that in bulk Cu(solid), versus the effective diameter of the Cu particle, down to the single-atom limit.

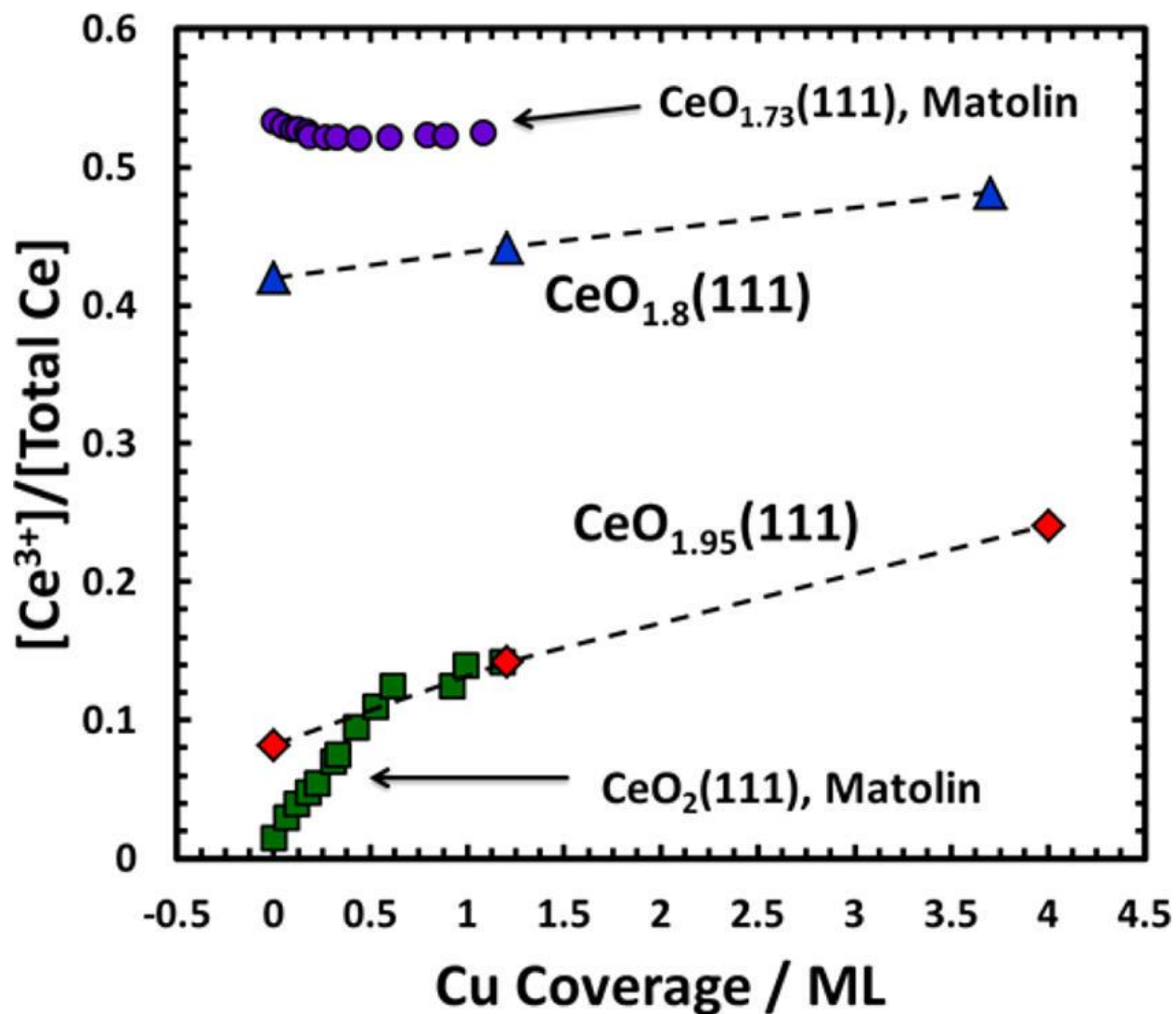


Figure 5.12. The Ce^{3+} contribution to the total Ce 3d XPS signal from $\text{CeO}_{2-x}(111)$ (determined by fitting the Ce 3d lineshape as in Figure 5.1), as a function of Cu coverage deposited onto $\text{CeO}_{1.95}(111)$ (diamonds) and $\text{CeO}_{1.8}(111)$ (triangles) at 300 K. Dashed lines are to aid the eye. Also shown for comparison are experimental data from Szabová and Matolin et al. for $\text{CeO}_2(111)$ that was initially fully oxidized (green squares) and heavily reduced (purple circles).

Table 5.1. Calculated heats of adsorption of isolated Cu adatoms on the most stable Cu adsorption site of CeO₂(111) using DFT+U compared to the experimental value, and the deviations from this experiment. To correct for the difference between enthalpies and energies, 0.8 kJ/mol (RT) was added to the calculated energies. Also listed are the U value and slab thickness used in each calculation, and the resulting charge on the Cu adatom. All calculations used a 2 x 2 cell. One trilayer is defined as an O-Ce-O trilayer.

ΔH_{ad} (kJ/mol)	ΔH_{ad} error (kJ/mol)	Cu charge	DFT functional	U (eV)	Slab thickness (trilayers)	Source
224±7	-	-	(EXPERIMENT)	-	-	This Work
293	69	1+	PBE	4.5	3	[¹⁷]
260	36	0.66+	PBE	5	3	[¹⁸]
254	30	1+	PBE	4.5	4	[¹⁹]
259	35	0.67+	PBE	5	2	[²⁰]
180	-44	0.70+	PW91*	5 then 3*	2	[²¹]*
270	46	0.71+	PW91	5		
336	112		LDA	5		

* Illas et al.²¹ pointed out that GGA tends to overestimate the CeO₂(111) lattice parameter, and so they used the local density approximation (LDA) with the functional of Vosko et al.⁴⁵ (VWN) with U = 5 for geometry optimization but used GGA with the Pedrew-Wang (PW91)⁴⁶ functional and U = 3 for energy and electronic calculations. They also performed pure GGA and LDA calculations for comparison, listed in the last two rows here.

Chapter 6. Trends in Adhesion Energies for Metal Nanoparticles Anchored onto Oxide Supports: Understanding Support Effects in Catalysis

This chapter contains unpublished results

Many catalysts consist of metal nanoparticles anchored to the surfaces of oxide supports. These are key elements in technologies for the clean production and use of fuels and chemicals. The chemical reactivity of the surface metal atoms on these nanoparticles is closely related to their chemical potential: the higher their chemical potential, the more strongly they bond small adsorbates. Controlling their chemical potential by tuning the structural details of the material can thus be used to tune their reactivity. As their chemical potential increases, this also makes the metal surface less noble, effectively pushing its behavior upwards and to the left in the periodic table. Also, when the metal atoms are in a nanoparticle with higher chemical potential, they experience a larger thermodynamic driving force to sinter. Calorimetric measurements of metal vapor adsorption energies onto clean oxide surfaces in ultrahigh vacuum show that the chemical potential increases with decreasing particle size below 6 nm, and, for a given size, decreases with the adhesion energy between the metal and its support, E_{adh} . The structural factors that control the metal/oxide adhesion energy are thus also keys for tuning catalytic performance. We present here new measurements of these adhesion energies and trends in how they vary with the metal and the support oxide.

6.1 INTRODUCTION

Metal nanoparticles dispersed across the surfaces of oxide and carbon supports form the basis for many catalysts and electrocatalysts of importance to future energy technologies, pollution

prevention and environmental protection, all necessary for any sustainable technological infrastructure that maintains a high quality of life. The activity and lifetime of such catalysts depends upon the details of their structure. The catalytic rate per surface metal atom and selectivity can vary with particle size when the metal particles are below about 7 nm in diameter,^{9,11,13–15,47,53,102,223,240,253–269} and on the choice of support and its extent of oxidation/reduction, even for particles of the same size.^{6,7,13,14,16,47,53,99,100,118,253,256,258,269–282} The Campbell group has shown previously that the chemical reactivity of the surface metal atoms on supported nanoparticles correlates with the chemical potential of the metal atoms in these particles⁵⁶: the higher their chemical potential, the more strongly they bond small adsorbates. As their chemical potential increases, the metal becomes less noble, effectively pushing its behavior to the left and up in the periodic table. Additionally, when the metal atoms are in a nanoparticle with higher chemical potential, they experience a larger thermodynamic driving force to sinter, and deactivate during use more rapidly via sintering.^{56,57} Our group further showed that the chemical potential increases with decreasing particle size below 6 nm,^{71,127} and, for a given size, decreases with the adhesion energy between the metal and its support, E_{adh} .⁵⁶ Thus, knowing how metal / oxide adhesion energies correlate with the properties of the materials used in making the catalysts is crucial for understanding and tailoring catalytic performance. This chapter presents a summary of experimental measurements of E_{adh} performed in the clean conditions of ultrahigh vacuum, and these adhesion energies are used to derive important trends that should allow predictive ability in how E_{adh} depends on the nature of the metal and of the support surface. These results and trends presented below will also provide important experimental benchmarks for validating the accuracy of quantum mechanical calculations that are used to estimate adhesion energies.

To quantify the relationship between adhesion energy and the chemical potential of metal atoms in supported metal nanoparticles, we draw on the relationship between the total internal energy U of a system consisting of a metal nanoparticle containing n moles of metal atoms attached to a support material in vacuum. The Campbell group has previously shown that⁵⁶:

$$U = n\bar{U}_{M,bulk} + U_{Sup} + \gamma_M A_M - E_{adh} A \quad (6.1)$$

where $\bar{U}_{M,bulk}$ is the molar internal energy of the pure, bulk metal (which we set to zero as the reference energy below), U_{Sup} is the total internal energy of the particle-free support before adhesion of the metal particle to it, γ_M is the surface energy of the metal/vacuum, A_M is the particle's total surface area, and A is the total area of metal / support contact. Both A_M and A depend on n . For a hemispherical nanoparticle, $A_M = 3\pi[3V_M/(2\pi)]^{2/3}n^{2/3}$, and $A = 1\pi[3V_M/(2\pi)]^{2/3}n^{2/3}$, where V_M is the molar volume of the bulk metal. In this case,

$$U = n\bar{U}_{M,bulk} + (3\gamma_M - E_{adh})(\pi[3V_M/(2\pi)]^{2/3})n^{2/3} + U_{Sup} \quad (6.2)$$

To semi-quantitatively show the effect of E_{adh} on metal chemical potential (μ_M), assume that both γ_M and E_{adh} do not vary with particle size (which is true for large particles, but not true below 6 nm^{35,39}), and that the molar entropy of the metal atoms does not depend strongly on particle size or support. In this case, the chemical potential, which is the partial derivative of the total free energy of the system (G) with respect to n , is given by:

$$\begin{aligned} \mu_M &= (\delta G / \delta n)_{T,P,etc} = (\delta G / \delta n)_{T,P,etc} \\ &= \bar{U}_{M,bulk} + (2/3)(3\gamma_M - E_{adh})(\pi[3V_M/(2\pi)]^{2/3})n^{-1/3} \end{aligned} \quad (6.3)$$

The first term ($\bar{U}_{M,bulk}$) drops to zero if the bulk metal is defined (for infinite size particles) as the reference state of zero energy or zero chemical potential. Thus, μ_M increases with γ_M and decreases with E_{adh} . As the adhesion energy increases, the metal's chemical potential decreases. Thus, *to understand how the chemical potential of metal nanoparticles depends on a catalyst's structural*

properties, we must understand how the adhesion energy depends on these properties. This chapter specifically addresses how E_{adh} depends on the metal element (for metals on the right side of the periodic table) and the oxide surface, for the case of well-defined single crystalline oxide surfaces.

6.2 AU ADSORPTION AND ADHESION ON MgO(100): COMPARISON TO OTHER METALS ON MgO(100) AND TO AU ON OTHER OXIDES

In addition to the metal / oxide systems described in this dissertation, previous work in the Campbell group revealed that metals from the right side of the periodic table (Cu, Ag and Pb) showed correlations between their measured heats of adsorption on MgO(100) and their bulk heats of sublimation, sticking probabilities, and film growth morphologies.⁶⁴ Like Au, these metals also grew as 3D clusters on MgO(100). Late transition metals are typically observed to nucleate at step edges when microscopy data are available.^{42,59,283–285}

At the lowest coverage studied in each case ($\approx 2\%$ of a monolayer), these metals are likely adsorbed at step and/or kink sites, likely already forming tiny, two- or three-dimensional clusters. Therefore, the measured *initial* heat of adsorption (meaning, the heat of adsorption of the first pulse of metal vapor) likely includes not only the bond energies of metal atoms to the step edges on MgO(100), but also some contribution from metal-metal bonding within the cluster. The initial heat of adsorption of Au on MgO(100) measured at 300 K (285 kJ/mol, see Chapter 4) is larger than the initial heats that the Campbell group previously measured for Pb (103 kJ/mol),⁶⁶ Ag (176 kJ/mol),⁶⁷ and Cu (240 kJ/mol)⁷⁴ on MgO(100). This fits with our group's observation that the initial heats of adsorption of metals on MgO(100) correlate with bulk cohesive energy.⁶⁴ Au has the largest bulk cohesive energy (368 kJ/mol), followed by Cu (337 kJ/mol), Ag (285 kJ/mol), and Pb (195 kJ/mol).¹⁸ The initial sticking probabilities of these four metals on MgO(100) at 300 K also increase with their initial heats of adsorption (and therefore, the bulk cohesive energy), and

as discussed in Chapter 4, sticking probability is related to the strength of metal monomer adsorption.⁶⁴ However, these two quantities (sticking probability and the heat of adsorption of the first pulse of metal atoms) depend on the size of particles formed in this first pulse, which depends on flux and particle saturation density. Because these initial heats are for particles of slightly different sizes, this trend is primarily qualitative rather than quantitative. It should also be noted that for Cu, Ag, and Pb, the saturation number densities of metal particles also was found to increase with the initial heats of adsorption (and therefore bulk cohesive energy),⁶⁴ however Au is the outlier in this case. The saturation number density of clusters for Au / MgO(100) is the *lowest* of any of these systems (see Chapter 4).

The adhesion energy of Au particles on MgO(100) measured here at 300 K is larger than the values determined calorimetrically for Ag and Cu at 300 K on MgO(100) (0.30 J/m² for a rough Au film,⁶⁷ 1.92 J/m² for a rough Cu film⁷⁴). While this follows the above trend for initial adsorption energies scaling with the heat of sublimation of the metal, it is in contradiction to the Campbell group's recently proposed trend for the adhesion energies of metals to oxide surface at the large-particle limit, where Au was predicted to fall below both Cu and Ag in adhesion energy (this trend will be discussed in detail below).⁵⁶ However, while the calorimetric adhesion energy for Au on MgO(100) at 300 K does not fit this trend, the adhesion energy determined at 100 K and the value derived from TEM measurements of particle shape,^{56,75,76} – both of which are for terrace sites on MgO(100) – fit the trend with Ag and Cu well. This implies that the adhesion energy of Ag and Cu on MgO(100) measured by calorimetry are also representative of terrace sites, which is reasonable as these values were determined for nearly-continuous films (that, in covering a large fraction of the MgO(100) surface, would include significant contributions from terraces, which are

in much higher concentration than step sites). In contrast, the calorimetry value for Au at 300 K is for *particles* that are localized on – and heavily influenced by – defects (see Chapter 4).

Compared to other oxides, MgO typically binds transitional metal nanoparticles weakly, while cerium oxide has been shown to bind transition metal nanoparticles very strongly, and to help them resist their sintering.^{39,57} Yet at 300 K, the initial heat measured here for Au on MgO(100) is ≈ 26 kJ/mol higher than the initial heat measured for Au on CeO_{1.95}(111),²⁰³ which would seem surprising given this trend. However, this is at least in part due to the difference in the initial size of the Au particles formed on these two surfaces. If we compare the heat of adsorption of Au on these two oxide surfaces at the smallest common particle size that we are able to measure (31 atoms), we find that at 300 K, Au particles on CeO_{1.95}(111) have a heat of adsorption that is ≈ 7 -10 kJ/mol higher than for 31-atom Au particles on MgO(100), which is consistent with ceria's stronger binding. However, the heat of adsorption of Au particles with ≈ 31 atoms on CeO_{1.95}(111) at 100 K is only ≈ 10 kJ/mol smaller than the value for particles of this size at 300 K,²⁰³ (compared to the 68 kJ/mol difference on MgO(100) for 100 K and 300 K). This suggests that topological defects play a much more significant role in the Au adsorption behavior on MgO(100) than they do on CeO_{1.95}(111). While the heat of adsorption of Au on MgO(100) reaches within 10 kJ/mol of the heat of sublimation of bulk Au(solid) by only ≈ 2 ML, these particles are already quite large by this coverage. At 2 ML, these Au particles are ≈ 3.2 nm thick, and have a diameter of ≈ 7.1 nm (2 ML coverage falls within the constant-diameter regime). This particle size is large compared to the particle size at which Au reaches within 10 kJ/mol of the heat of sublimation of bulk Au(solid) on CeO_{1.95}(111), which occurred at a hemispherical particle diameter of only 3.2 nm.²⁰³ This can only be true if Au binds more strongly to CeO_{1.95}(111). It was previously observed that Ag nanoparticles reached the heat of sublimation of bulk Ag(solid) at smaller particle sizes on

CeO_{1.95}(111) than on MgO(100), which was also consistent with stronger binding of Ag to CeO_{1.95}(111), and the observation that ceria maintains small metal particles better than other oxides like MgO due to stronger binding.^{39,203} This trend appears to hold for Au here as well.

Both Ag³⁹ and Cu¹²⁶ had stronger adhesion to CeO_{1.95}(111) than to MgO(100) by ≈ 2 J/m². Yet the adhesion energy that we measured for 3.6 nm diameter hemispherical Au particles on CeO_{2-x}(111) was 2.53 J/m²,²⁰³ which is only ≈ 0.3 J/m² larger than the value found here for 7.1 nm diameter disk-shaped Au particles on MgO(100) defects at 300 K. However, the adhesion energy of Au particles on CeO_{1.95}(111) is ≈ 2 J/m² larger than the much lower adhesion energy found at 100 K for Au particles on MgO(100) terraces.

These results consistently support the observation that MgO(100) binds Au more weakly than CeO_{1.95}(111), but that Au is far more sensitive to the presence of morphological defects on MgO(100) than on CeO_{1.95}(111). To review, this conclusion is built on the following four comparisons:

- 1) The particle density measured at 300 K for Au on MgO(100) is nearly an order of magnitude smaller than on CeO_{1.95}(111) at 300 K. Smaller particle densities arise from monomers that diffuse more rapidly because they are bound more weakly to the surface, as the diffusion activation barrier correlates with the strength of monomer adsorption.
- 2) In analyzing the mass spectrometer pulse lineshape from the Au atoms that adsorb but do not stick (see Chapter 4), we measured an upper limit for the Au monomer adsorption energy on MgO(100) of 64 kJ/mol at 300 K and 22 kJ/mol at 100 K. This extremely weak Au monomer binding energy *must* be lower than the binding energy of Au monomers to the CeO_{1.95}(111) surface, given that the sticking probability of the

- first pulse was >99% on CeO_{1.95}(111) at 300 K (compared to only ≈90 % on MgO(100)), and the heat of adsorption of this first pulse was 255 kJ/mol for particles that are 1-2 atoms in size on CeO_{1.95}(111) at 100 K, which is an order of magnitude higher than the upper limits found here for Au monomer adsorption on MgO(100).
- 3) For particles that contain approximately the same number of Au atoms (31 atoms), the heat of adsorption on MgO(100) is ≈10 kJ/mol smaller than the heat of adsorption on CeO_{1.95}(111). However the difference between the heat of adsorption of particles of this size at 300 K compared to 100 K is much larger on MgO(100) than on CeO_{1.95}(111).
 - 4) The adhesion energy of Au particles on MgO(100) measured by SCAC in the large-particle limit is smaller than for Au on CeO_{1.95}(111), even though the particle size is larger for MgO(100). This adhesion energy trend will be discussed in the next section.

6.3 TRENDS IN METAL / OXIDE ADHESION

As noted in previous chapters, the adhesion energy between a multilayer metal film or metal nanoparticle and the underlying oxide surface can be determined from the integral heat of metal adsorption on the oxide.^{42,67,72} On MgO(100), the calorimetrically measured adhesion energies of these metals in their large-size limit (either large particles or rough films) determined by the Campbell group prior to the work presented in this dissertation are: Pb = 0.57 ± 0.2 J/m², Ag = 0.30 ± 0.3 J/cm², and Cu = 1.92 ± 0.5 J/m² (see Table 6.1). Unlike the initial heats of adsorption of these three metals (see above), the adhesion energies do *not* increase with the bulk sublimation enthalpy. One possible explanation for the higher value for Pb compared to Ag may be related to the fact that Pb–O bonding is much stronger than Ag–O bonding, as evidenced by the much larger heat of formation (per mole metal) for the most stable bulk oxide of Pb than for that

of Ag.¹⁸ This suggests that local chemical bonds, both metal–oxygen and covalent metal–magnesium, dominate the interfacial bonding.

Table 6.1 shows a summary of metal / oxide adhesion energies that have been measured recently with metal adsorption calorimetry, including the work from this dissertation as well as data collected by previous members of the Campbell group (including those values on MgO(100) described above). This information is presented together with other metal / oxide adhesion energies that have been reported from experimental measurements of the metal nanoparticle shape, along with citations to the references where these previously-published data are found. In all cases, these values of adhesion energy are for solid metal nanoparticles or films prepared by metal vapor deposition in the clean conditions of ultrahigh vacuum. The surface cleanliness was verified in each case either directly before metal deposition, or in identical control experiments. This is important, since surface impurities are known to have a strong influence on the metal / oxide interfacial bond strength.⁸⁶ For example, the value of E_{adh} for Cu(solid) on $\alpha\text{-Al}_2\text{O}_3(0001)$ in Table 6.1 is 2.8 J/m^2 that was obtained from ultrahigh vacuum measurements greatly exceeds the value of $0.61 \pm 0.11 \text{ J/m}^2$ reported for this same interface based on measurements in a much less clean environment.²⁸⁶

It is also important to note that these adhesion energies reported from SCAC measurements are all for either continuous films, or for hemispherical particles at 35% surface coverage (the large-particle limit). This means that the adhesion energy is calculated for different particle sizes, however these particles are at their large-size limit (just before they begin to overlap), and adhesion energy should not vary more than $\approx 10\%$ above this size

Figure 6.1 shows that, for a given oxide surface, the adhesion energies for different metals correlate with the strength of bonds that metal atoms make to oxygen atoms. The data for E_{adh} are

plotted versus $[(\Delta H_{\text{sub,M}} - \Delta H_{\text{f,MOx}})/N_A]/\Omega_M^{2/3}$ in Figure 6.1, where $\Delta H_{\text{sub,M}}$ is the metal's bulk sublimation enthalpy (per mole of metal), $\Delta H_{\text{f,MOx}}$ is the heat of formation of the most stable oxide of the metal (per mole of metal), N_A is Avagadros number and Ω_M is the atomic volume of the bulk solid metal. This quantity $\Delta H_{\text{sub,M}} - \Delta H_{\text{f,MOx}}$ equals the heat of formation of the metal's most stable oxide from a metal gas atom plus $\text{O}_2(\text{g})$, so it directly reflects the strength of the chemical bonds which each metal can make to oxygen. This is a far better way to estimate how strongly different metal surfaces can bond to the oxygen anions on the surface of an oxide than $\Delta H_{\text{sub,M}}$ alone. The denominator ($\Omega_M^{2/3}$) is approximately the surface area per metal atom, so it normalizes this energy to the interfacial area (instead of per metal atom).

As seen in Figure 6.1, the correlation of E_{adh} with $[(\Delta H_{\text{sub,M}} - \Delta H_{\text{f,MOx}})/N_A]/\Omega_M^{2/3}$ is very strong, and essentially linear for both $\text{MgO}(100)$ and slightly reduced $\text{CeO}_{1.95}(111)$. These two lines share the same slope of 0.14. This correlation was shown previously by Sellers and Campbell for $\text{MgO}(100)$ based on a more limited data set.⁵⁶ When this correlation was first reported for metal adhesion on $\text{MgO}(100)$,⁵⁶ we proposed that relating E_{adh} to the oxophilicity of the metal atom made physical sense because the dominant contribution to the bonding between the metal surface and the oxide lattice surface is from the bonds between the metal atoms in the particle and the oxygen anions of the oxide. This is based on the fact that DFT calculations generally prove that late transition metal adatoms on stoichiometric oxide terraces prefer to bind to oxygen anions rather than cations (see, for example, References 51, 119, 120).

The heat of adsorption of isolated metal monomers was reported for Au and Cu on $\text{CeO}_{1.95}(111)$ in Chapters 3 and 5, and was found to be 209 and 223 kJ/mol, respectively.^{127,203} These are in a ratio of Cu/Au of 1.07, which is similar to the ratio of their adhesion energies from Table 6.1 and Figure 6.1: $\text{Cu/Au} = 3.52/2.53 = 1.39$. This $\text{CeO}_{2-x}(111)$ surface had $\approx 5\%$ percent

step sites and $\approx 2.5\%$ oxygen vacancies, mainly located at these steps sites. Due to the low temperature of these studies (100 K), these monomers were determined to be mainly at terrace sites (since the heat of adsorption was much higher at 300 K where they could diffuse to step edges, although some contribution from terraces may be present in this Au value, since Au is much more mobile than Cu^{217,280,287}). Quantum mechanical calculations of both Au and Cu monomers on CeO₂(111) show that they bind on top of surface oxygen atoms of the oxide lattice.^{112,115,150,228} Thus, both these ratios reflect the relative strength of metal-oxygen bonding. However, both ratios are much smaller than the Cu/Au ratio in the x-axis of Figure 6.1, which is $15.87/9.024 = 1.76$. This much larger ratio suggests that metal binding to oxide surfaces, whether as metal monomers or metal particles, is much more complicated than the binding of those same metal atoms to *free* oxygen atoms when making its metal oxide.

This trend for metals seems to match preliminarily (at least qualitatively) with the predictions of DFT, though there has not been a comprehensive systematic study that covers all of the systems presented in Figure 6.1. The calorimetrically-determined adhesion energy of Au to CeO_{1.95}(111) is larger than the adhesion of Ag³⁹ and smaller than the adhesion of Cu¹²⁶ as predicted by this proposed trend, however this is contrary to DFT calculations by Branda et al.,³¹ which predicted that Au binds the most weakly to ceria than both Ag and Cu. This might be explained by the fact that these authors showed that their results for Au were highly method dependent. For example, while all DFT methods tested predicted that Cu and Ag would form Cu⁺ and Ag⁺ on ceria, these same methods predicted a variety of negative, neutral, and positively charged Au, and this method-dependency may be the source of this adhesion energy trend disparity. Siculo et al.²¹¹ calculated that metals on bulk-like MgO(100) obey the following order in monomer adsorption energy: Pt > Ni > Pd > Cu > Au > Ag. While these do not quite match the trend proposed here (Ni

is predicted to be higher than Pt), there is actually reasonable qualitative agreement for the case of the other metals discussed here.

Note that the trend lines for MgO(100) and CeO_{1.95}(111) in Figure 6.1 are parallel to each other, but offset by a large amount. This offset appears to be independent of the nature of the metal. It is as if the change from MgO(100) and CeO₂(111) allows the metal-oxygen interfacial bonds to all get stronger by essentially the same amount, nearly independent of the oxophilicity of the metal particle. The fact that the lines in Figure 6.1 for MgO(100) and CeO_{1.95}(111) are nearly parallel suggests that all oxides of the type used for catalyst supports are probably roughly parallel on this plot. Therefore, in Figure 6.1, we have added points for the measurements on single-metal elements that have been made for several other oxide surfaces in the clean conditions of UHV (from Table 6.1). This trend, if indeed essentially parallel as drawn for all binary oxide surfaces of this type, may have the potential to predict for a wide variety of metal / oxide adhesion energies. For the case of α -Al₂O₃(0001), a dashed line is drawn through the point for Cu adhesion with this same slope of 0.14 to show the potential predictive power of this trend.

One can see that for a given metal, the adhesion energy to the oxides ranks in increasing magnitude as: MgO(100) $\approx$ TiO₂(110) < α -Al₂O₃(0001) < CeO₂(111) $\approx$ Fe₃O₄(111). This order is consistent with the trend estimated previously,⁵⁶ based on more limited data, which gave: MgO(100) $\approx$ TiO₂(110) $\leq$ α -Al₂O₃(0001) < CeO₂(111) $\leq$ Fe₃O₄(111). Recognizing that the trends in Figure 6.1 for MgO(100) and CeO_{1.95}(111) are nearly parallel greatly increases our confidence in the accuracy of this ranking.

We propose that the physical origin of this ranking, i.e., the reason for the offsets in the lines in Figure 6.1 for different oxides, is related to the chemical potential of metal anions in the oxide surface. The adhesion energy of the same (or similar) molten metals on different oxides (in

unclean environments) were shown to decrease with the magnitude of the heat of formation (or stability) of the oxide per mole of O.⁵⁶ This was explained as follows⁵⁶: The oxide substrates with the least negative heats of formation per mole of O have the highest chemical potential of oxygen atoms in their oxide lattice. The higher the chemical potential of the surface oxygen atoms in an oxide lattice, the more strongly these atoms can bond to the metal atoms of a metal surface to which it attaches. As noted above, the dominant contribution to the interfacial bonding between the metal surface and the surface of the oxide lattice is from the bonds of the metal atoms to the surface oxygen anions of the oxide lattice, and not to the lattice cations. Thus, the more weakly bound a surface oxygen ion is to its neighboring cations within the oxide lattice, the stronger should be the bond it makes to a metal atom or metal particle that approaches its surface.

Unfortunately, the y-axis offsets in Figure 6.1 for clean oxide surfaces do *not* correlate with the heat of formation of the oxide (per mole of oxygen). This may be due to the fact that the actual chemical potential of an oxygen atom in an oxide single-crystal surfaces does not correlate so directly with the heats of formation of the bulk oxide. The oxygen atom stability in the oxide surface's outermost atomic layer probably depends critically on the structural details of that surface facet, its surface energy, and to what extent it has been reduced by annealing in vacuum or oxidized by treatment in oxygen.

It seems likely that the oxygen chemical potential may correlate better with the oxygen *vacancy formation* energy. To our knowledge, no group has compared the oxygen formation energies of more than 2-3 of these oxide surfaces presented in Figure 6.1 using the same DFT conditions. However, a preliminary investigation of the literature suggests that the oxides with the lowest y-axis intercept have the highest energies of vacancy formation. For example, the typical range of vacancy formation energies calculated on MgO(100) is 9-11 eV^{220,222,288,289}, while for

CeO₂(111) and Fe₃O₄(111), typical oxygen vacancy formation energies are 2-4 eV.^{117,290–293} The available DFT for Al₂O₃(0001) have a broader spread, as they depend on the surface termination (Al- or O- terminated), and what layer the oxygen is being removed from, but they seem to fall within the range of 6-10 eV,^{294,295} again qualitatively agreeing with what we expect from the y-axis offset. The only outlier is the TiO₂(110) surface, which is reducible, and should therefore have an oxygen vacancy formation energy that is similar in magnitude to the other two reducible oxides (Fe₃O₄(111) and CeO₂(111)), but instead the line on our adhesion trend falls close to MgO(100). A preliminary investigation into the DFT literature suggests that the energy of vacancy formation is in the range of 3-5 eV,^{296,297} however many of these values come from the energy to remove an O⁻ or O²⁻, and the energy to remove a neutral O may in fact be much higher. For example, when Wang et al.²⁹⁷ modeled this surface, they found that the energy to remove a neutral oxygen atom was ≈ 8 eV, compared ≈ 4.5 eV for O⁻. Since we are proposing that this trend is related to the chemical potential of O *atoms* (not ions) in the oxide lattice – in other words, the ability of these O atoms to “react” with the metal particles – it makes more sense to consider the energy to remove a neutral oxygen atom. While a comprehensive DFT comparison is needed to investigate this trend further (using the same model, relaxation conditions, and DFT functionals), this is a promising line of reasoning to explain the relative adhesion energy offsets in Figure 6.1.

Finally, note that oxygen vacancies increase E_{adh} for Ag and Au on CeO₂(111), but not for Cu. Therefore, the adhesion energy trend line for CeO_{1.80}(111) seems to lie slightly above the line for CeO_{1.95}(111), but with a smaller slope. However, perhaps a better way to discuss these data is consider them as representing two different surfaces – the Ag and Au “see” a vacancy-rich ceria surface, while the Cu is not affected by these vacancies, and therefore “sees” a defect-free surface. Therefore, it is perhaps incorrect to connect these data with a single line, and instead consider the

Cu /CeO_{1.80}(111) point as part of the CeO_{1.95}(111) dataset, and consider the Ag and Au points on CeO_{1.80}(111) as their own line describing vacancy-rich ceria surfaces.

6.4 CONCLUSIONS

This chapter reviews metal adsorption and adhesion onto MgO(100), CeO_{2-x}(111), and other single crystal oxide surfaces measured experimentally using SCAC or particle-shape techniques. In general, CeO_{2-x}(111) binds metals more strongly than MgO(100), but the role that electron-rich morphological defects (such as steps) play in metal adsorption on MgO(100) appears more influential than it is on CeO_{2-x}(111). This latter observation is based on the strong difference in measured Au adsorption and adhesion energies at the same particle sizes at 100 K on MgO(100). A systematic trend is proposed between the adhesion energy of nanoparticles at the large-size limit onto oxide surfaces in UHV and the sum of the magnitudes of the metal's heat of sublimation plus the standard heat of formation of the most stable bulk oxide of that metal (per mole of metal atoms). This trend was initially proposed *only* for MgO(100),⁵⁶ and in this work it has been extended to include other oxide surfaces using both data presented in this dissertation and other UHV data from the literature. In the case of CeO_{1.80}(111), the behavior of oxygen vacancies influences metal adsorption in different ways depending on the metal – for example whereas Ag and Au bind more strongly to oxygen vacancies, Cu does not. Therefore, it is reasonable to argue that rather than a single line with a lower slope, this dataset represents two different surfaces (a vacancy-rich ceria surface and a defect-free surface). This trend may be applicable for metal adsorption to other oxides, and may offer a predictive trend in determining adhesion energy.

6.5 FIGURES

Table 6.2. Adhesion energies of solid metals measured on clean oxide surfaces under ultrahigh vacuum conditions. Methods used are based either on the particle shape (HRTEM and GISAXS) or on the integral heat of adsorption of metal vapor at multilayer coverage (SCAC). All data are from the citations listed, but the values marked with an asterisk have been recalculated based on newer values for the surface energies of the pure metals reported in Reference ²⁹⁸. Also listed is the heat of formation of the most stable bulk oxide of that metal (per mole of metal atoms), $\Delta H_{f,MOx}$.

metal	oxide	particle size / nm	E_{adh} (J/m ²)	$E_{adh} / 2\gamma_{v/m}$	$\Delta H_{f,MOx}$ / (kJ/mol M)	method	citation
Pb	MgO(100)	10+	0.57*	0.65	-219	SCAC	66
Ag	MgO(100)	6.6	0.30	0.12	-15.1	SCAC	67
	CeO _{1.9} (111)	3.6	2.3	0.94		SCAC	39
	CeO _{1.8} (111)	3.6	2.5	1.0		SCAC	39
	Fe ₃ O ₄ (111)	3.6	2.5	1.0		SCAC	71
Au	MgO(100)	1-5	0.67*	0.22	9.65	HRTEM	76
	MgO(100)	7	0.31	0.10		SCAC	Ch. 4
	TiO ₂ (110)	2-8	0.54*	0.18		GISAXS	299
	TiO ₂ (110)	>4	0.71*	0.24		HRSEM	300
	CeO _{1.95} (111)	3.6	2.53	0.84		SCAC	Ch. 3 ²⁰³
	CeO _{1.80} (111)	2.5	2.83	0.94		SCAC	Ch. 3 ²⁰³
Pd	MgO(100)	10-15	1.11*	0.28	-85.4	HRTEM	301
		2-8	1.34*	0.34		GISAXS	302
Cu	MgO(100)	10+	1.92	0.55	-168.2	SCAC	74
	CeO _{1.95} (111)	2.2	3.52	0.98		SCAC	Ch. 5 ¹²⁶
	CeO _{1.90} (111)	2.2	3.45	0.96		SCAC	Ch. 5 ¹²⁶
	CeO _{1.80} (111)	2.2	3.43	0.96		SCAC	Ch. 5 ¹²⁶
Pt	MgO(100)	1-5	1.51*	0.30	-54.3	GISAXS	303

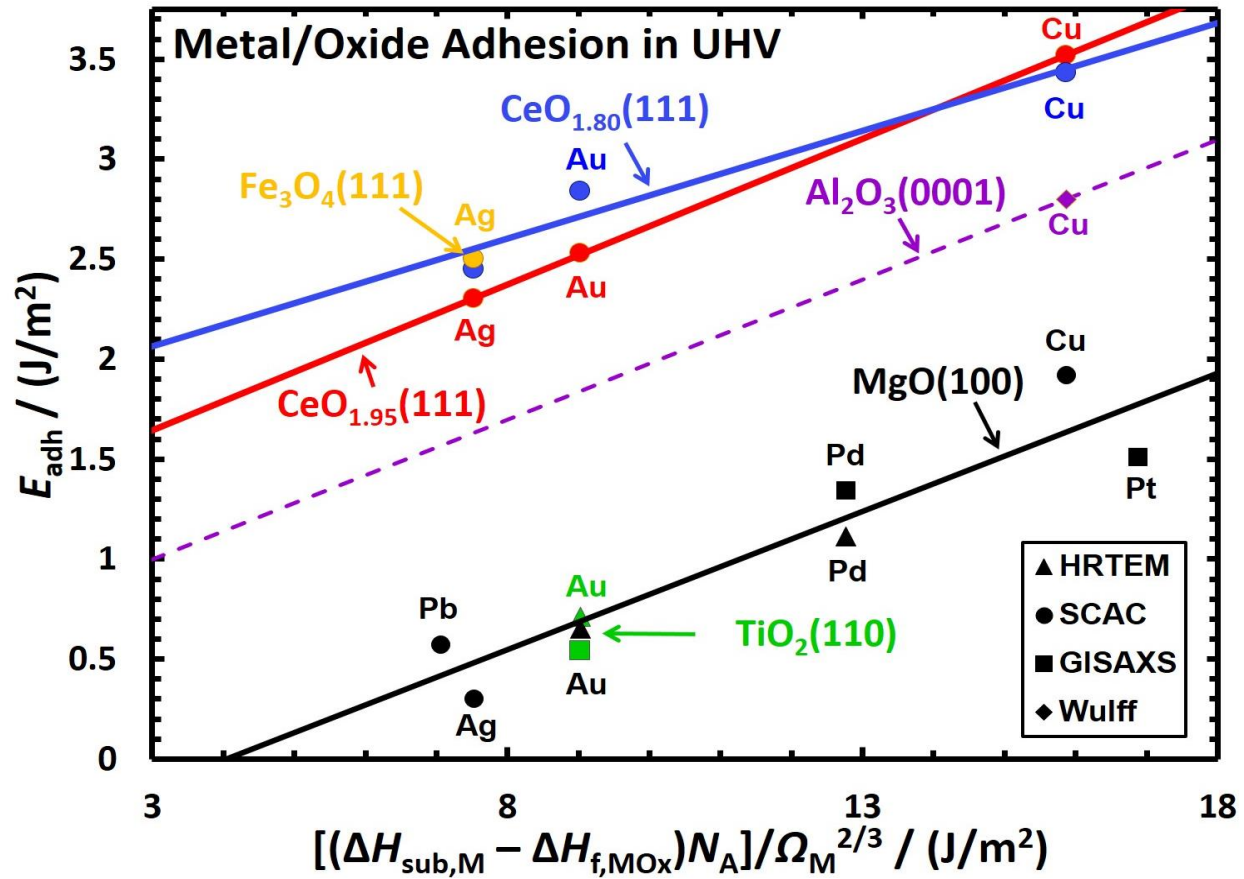


Figure 6.1. UHV-measured adhesion energies of various systems of metals on oxides at the large-particle or continuous-film limit. These adhesion energies are plotted versus the bulk metal's sublimation enthalpy minus the heat of formation for the metals most stable oxide divided by the area per metal atom. The oxides shown, which are discussed in detail this dissertation, are MgO(100) (black), CeO_{1.95}(111) (red), and CeO_{1.80}(111) (blue). The data determined calorimetrically by the Campbell group is shown as circles, and other UHV techniques from the literature are shown as triangles (HRTEM) squares (GISAXS) or diamonds (Wulff particle shape analysis). The lines through the data are best linear fits to all UHV data. The trends for MgO(100) and CeO_{1.95}(111) have approximately the same slope (0.14), while CeO_{1.80}(111) has a lower slope, which is due to the lower relative adsorption energy of Cu on the more reduced surface. Using the slope from the black and red lines, we can extrapolate a linear trend based on only a single data point from different systems of metals on other oxides in UHV. One such example is shown here in purple for Al₂O₃(0001).

Chapter 7. Model Bimetallic Catalysts: The Adsorption of Au and Cu Layers on Pt(111)

This chapter contains unpublished results

This chapter describes the use of single-crystal adsorption calorimetry (SCAC) to measure interfacial energetics of vapor-deposited Cu and Au films onto Pt(111) at 300 K. For Cu, the heat of adsorption decreases linearly as the first monolayer is deposited. This result is consistent with Cu adsorbing more strongly to Pt step edges than Cu step edges. The heat of adsorption continues to decrease until a coverage of 2.5 ML where it reaches 333 kJ/mol, which is consistent with Cu adsorbed to a strained Cu overlayer more weakly than it would to Cu(bulk). This result also shows that Cu-Cu bonds are less energetically favorable than Cu-Pt bonds. The linear decrease in heat is explained as an energy penalty from lattice strain and island-island repulsion within the first monolayer. As the Cu coverage approaches 3 ML, the heat of adsorption increases to, and remains constant once reaching, the Cu(bulk) heat of sublimation.

For Au, the heat of adsorption increases linearly from 382 kJ/mol to 393 kJ/mol within the first 0.03 ML, and then remains constant until 0.7 ML. From 0.7 – 1 ML, the heat of adsorption decreased linearly to the Au(bulk) heat of sublimation. As with the Cu results above, this result for Au shows that Au binds more strongly to Pt step edges than to Au. The two systems differ in that Au has a much smaller energy penalty that does not become significant until the islands reach a certain size. This pattern of rise-level-fall in the heats of adsorption is repeated from 1 - 2 ML and from 2 - 3 ML, but in each additional layer, the constant adsorption energy value is smaller, at ≈ 374 kJ/mol and ≈ 371 kJ/mol respectively.

The adhesion energy of Cu and Au films onto Pt(111) was measured calorimetrically as described previously. The adhesion energy of Cu to Pt(111) decreases as the Cu film becomes thicker between 1 and 4 ML from 3.84 to 3.76 J/m², while conversely, the adhesion energy of Au onto Pt(111) increases as the film becomes thicker from 3.57 to 3.74 J/m². This difference is likely due to the energy penalty paid by a strained first Cu layer compared to a significantly less strained first Au layer on Pt(111), which is due to a difference in atomic size. Finally, the heats of adsorption of Cu are compared to previous experimental and theoretical results showing that environment (i.e. solvent effects) and specific surface structure dramatically affect the measurement and calculation of these types of energies.

7.1 INTRODUCTION

Bimetallic catalysts generally have physical, chemical, electronic, and catalytic properties that are unique from their individual parent metals,^{53,304–306} and thus they often exhibit superior performance as catalysts and electrocatalysts.^{53,304–309} In order to understand how the choice of metal influences the catalytic properties of a bimetallic system, a variety of detailed surface science studies have been performed where the structure, total concentration of each metal, and cleanliness of the system can be controlled.^{53,304–307} Fundamental studies of this type can lead to the development of more efficient, environmentally friendly catalysts. Whereas true alloys are often excellent catalysts and have been used for decades, a newer class of bimetallic catalysts that has shown particular promise involve core-shell nanoparticles, where one metal element exists as a single monolayer coating the surface of the second metal.^{153,310,311} Whereas the thermodynamics of alloy formation have been well studied,³⁰⁶ much less is known about the energetics of such monolayer metal films on another metal's surface. For two metals that are immiscible in the bulk,

the heat of adsorption of one metal on another has been measured by temperature programmed desorption (TPD) in many cases,³⁰⁶ and once by SCAC.⁸³ However, for two metals that can form a bulk alloy, the heat of adsorption of a single layer of an adsorbed metal has never been measured on the other metal, because TPD does not work for such systems where the metals alloy before reaching the desorption temperature. The first such energetic measurements for systems of this type are reported here for the adsorption Cu and Au layers on Pt(111).

Alloying Cu or Au with Pt has proven to be an effective way to tune the catalytic properties of Pt. Basic research has focused heavily on models of CuPt or AuPt systems as prototypes in basic research aimed at elucidating the relative importance of electronic effects versus ensemble effects in bimetallic catalysis.^{304,305,312–314} Well-ordered Cu overlayers and thin-film CuPt alloys grown on Pt(111) are examples of model systems that are used to clarify how these effects relate to the unique adsorption properties of CuPt bimetallics, which in turn relates to their catalytic properties involving small molecules such as oxygen,³¹⁵ CO,^{316,317} CO₂,^{318,319} and formate.³²⁰ Sachtler and Somorjai investigated a related system of overlayers of Au on Pt(111) and Pt(100), and found enhanced catalytic properties compared to single-crystal Pt surfaces.^{312,313,321–323} Similarly, Pt layers deposited on Au(111) show increased reactivity compared to single-metal Pt or Au, as determined by CO TPD.³²⁴

To gain the first insight into the energetics of metal-metal bonding at the interface of core-shell bimetallic catalysts particles consisting of *miscible* metals, the adsorption and adhesion energies of vapor-deposited Cu and Au onto clean, well-ordered Pt(111) at 300 K was investigated by single-crystal adsorption calorimetry (SCAC). Even though Cu and Au fall in the same column of the periodic table, they often have dramatically different chemical and physical properties, for example their size, electronic characteristics, acid-base properties, and reactivity. Cu (atomic

radius ≈ 1.28 Å) is smaller than Pt (atomic radius ≈ 1.39 Å), whereas Au is larger than Pt (atomic radius 1.44 Å). This small difference in size can have enormous effects on the way that admetal layers grow on another metal. The calorimetric data presented here provide a direct comparison between two systems of high significance in the field of bimetallic catalysis through a thermodynamic and structural lens. The adsorption energies presented here are interpreted in light of previous detailed structural analyses of Cu adsorbed on Pt(111)^{325–328} and Au adsorbed on Pt(111).^{313,321,329} The work presented in this chapter marks only the second and third bimetallic system adsorption directly measured by SCAC, respectively.^{83,330} Adsorption energies of Cu and Au onto other transition metals have been previously been reported using temperature programmed desorption (TPD),^{60,306,331} but could not be measured for Cu or Au on Pt since annealing causes these metals to alloy with Pt before they desorb.^{313,324,332–335}

The growth of vapor-deposited Cu on Pt(111) has been studied in detail by Auger electron spectroscopy (AES),^{326,328} low-energy electron diffraction (LEED),^{326,328} thermal desorption spectroscopy (TDS) of H₂ and CO,^{326,328} and scanning tunneling microscopy (STM).³²⁵ Cu grows layer-by-layer on Pt(111) in the first monolayer (ML). This result is supported by two lines of evidence. First, there is linear decrease in the saturation coverage of H and CO (by TPD) with Cu coverage to nearly zero in the first ML. Second, there is a distinct break in the Cu and Pt AES signals at 1 ML.^{326,328} STM results are also consistent with Cu growing layer-by-layer, with nucleation occurring primarily at Pt step edges followed by the formation of branched Cu islands.³²⁵ The branching was attributed to large diffusion lengths of Cu monomers on Pt(111) terraces, and slow diffusion of Cu atoms along the edges of the Cu islands that nucleate and grow. During the growth of the first Cu layer, no nucleation was seen on terraces. Growth occurred only at Pt(111) step edges, indicating that Cu-Pt bonds are stronger than Cu-Cu bonds.³²⁵ Early LEED

results showed that Cu growth is pseudomorphic with Pt(111) as evidenced by the appearance of no new LEED spots at the highest submonolayer coverage studied ($\approx 1/2$ ML).^{326,328} When the second Cu layer was deposited, new LEED spots were observed with an $\approx 8\%$ smaller lattice parameter, indicating Cu grew with the ideal Cu(111) lattice spacing in the second and subsequent layers.³²⁶ However Miszczuk et al.³²⁷ used LEED and directional elastic peak electron spectroscopy (DEPES) to find that Cu is not entirely pseudomorphic, but instead forms a misfit Cu(13 x 13) layer on Pt(12 x 12) at a coverage just over 1 ML at 330 K, which is consistent with a lattice parameter very near that of Cu(111). (Note that the Cu coverages were all reported by Miszczuk et al. as 1/2 of their true values, based on comparison of the Cu/Pt peak ratio in AES to those reported in Ref. ³²⁶, where CO and H chemisorptions clearly identified monolayer completion).

The growth of epitaxial Au thin-films on Pt(111) by vapor deposition has been studied using Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED), and thermal desorption spectroscopy (TPD) of CO.³¹³ AES shows distinct breaks at the successive completions of the first three monolayers in the Auger signal versus time of deposition, indicating layer-by-layer growth similar to Cu. TPD exhibited a linear decrease in the CO adsorbed as a function of Au deposited, which supports layer-by-layer growth. Moreover, the position of the break agrees with the single-layer coverage point as determined by AES.³¹³ The growth of Au layers is also similar to the growth of Cu layers in that Au growth is pseudomorphic with Pt(111) as evidenced by the appearance of no new LEED spots within the first monolayer of Au deposition. However, whereas Cu grew with its ideal (111) spacing by the time it formed a second layer (as indicated by new LEED spots with an 8% smaller lattice parameter appearing³²⁶), multilayers of Au did *not* produce to any new spots beyond the Pt(111) hexagonal pattern, even after annealing the system

at temperatures as high as 1270 K. The sharpness of the Pt(111) diffraction spots decreased slightly after several layers of Au were deposited, and a continuous increase of the lattice constant of the clean Pt(111) surface toward that of Au(111) was observed (as calculated from the spot-to-spot distances), which was spread out over five or more monolayers. It is clear from these results that Au layer growth on Pt(111) is substantially different from that of Cu, which is likely due to the fact that Au is larger than Pt (and closer in size), whereas Cu is smaller.³¹³

7.2 EXPERIMENTAL DETAILS

A 1 μm Pt(111) single-crystal, purchased from Jacques Chevallier of Aarhus University, was cleaned by successive cycles of 1 keV Ar^+ sputtering in 6×10^{-6} background Ar, followed by annealing to 1173 K in UHV, then to 873 K in 1×10^{-6} Torr O_2 until no C was present as measured by XPS. A final flash to 1173 K in UHV for 1 minute immediately before calorimetry experiments removed any residual oxygen. Sample order was verified by sharp Pt(111) LEED spots. After deposition of metal (either Cu or Au) for calorimetry, the sample was first cleaned by 1 keV Ar^+ sputtering in 6×10^{-6} Ar until no admetal was present in XPS. This step prevented Pt alloying during the annealing steps.

The absolute calibration factor was scaled slightly so that the multilayer heat of adsorption in the high-coverage limit equals the literature value for the heat of sublimation of bulk Cu(solid) from Reference 34. The total admetal coverage is recorded in monolayers (ML), where 1 ML = 1.5×10^{15} atoms/ cm^2 which is the atomic density of Pt atoms in the (111) surface.

7.3 RESULTS

All heats of adsorption reported here have been corrected slightly for the elevated temperature and collimated nature of the atomic beam as described previously (see Chapters 3-6).

As a result, the heats correspond to Cu or Au atoms in a Boltzmann distribution at the surface temperature, and the values presented here correspond to the standard enthalpy of adsorption at the sample temperature multiplied by -1.

Figure 7.1 shows the heat of adsorption for vapor deposited Cu onto Pt(111) as a function of Cu coverage at 300 K. These data are divided into three distinct regions based on the growth of Cu on Pt(111) described above. In region 1 (0-1 ML), Cu adsorbs with an initial heat of adsorption of 357 kJ/mol. The heat of adsorption decreases over the first 1 ML to reach 339 kJ/mol by 2 ML coverage. Figure 7.2 shows the heat of adsorption in region 1 in additional detail. The decrease in heat of adsorption is well fit by a linear decrease that follows the equation $\Delta H_{\text{ads}} = (358 - 19\theta)$ kJ/mol, where θ is the total Cu coverage in ML. In region 2 (1-3 ML), the heat of adsorption continues to decrease, and reaches a minimum of ≈ 335 kJ/mol between 1.5 and 2.5 ML. The heat then increases to the heat of sublimation of bulk Cu(s), 337 kJ/mol,¹⁸ by 3 ML. Above 3 ML, the heat of adsorption remains constant at 337 ± 3 kJ/mol

The heat of adsorption of Au on Pt(111) is shown in Figure 7.3. These data have similarly been divided into the same approximate regions of coverage as for Cu in Figure 7.1, with the first region shown in additional detail in Figure 7.4. In region 1 (0 - 1 ML) the Au atoms are initially adsorbed with a heat of 382 kJ/mol, and there is a sharp rise in adsorption energy up to a coverage of 0.03 ML unlike for Cu (Figure 7.1). From 0.03 to 0.7 ML, the energy remains constant at an average value of 393 ± 5 kJ/mol. Above 0.7 ML until the completion of the first monolayer, the Au adsorption energy drops linearly to that of the bulk heat of sublimation of Au(s) (368 kJ/mol¹⁸). In region 2 (1 - 3 ML) the adsorption energy again rises linearly from the bulk head of sublimation to ≈ 374 kJ/mol, where it remains constant from 1.3 - 1.8 ML, and then again linearly decreases back to the bulk heat of sublimation of Au by 2 ML. This pattern of rise-level-fall is repeated again

from 2 - 3 ML, but the constant adsorption energy value is once again smaller, only reaching ≈ 371 kJ/mol. Finally, in region 3 (3 ML and above) the adsorption energy remains constant at the bulk heat of sublimation of Au.

From the heats versus coverage data in Figure 7.1 and Figure 7.3, the adhesion energy of Cu(solid) to Pt(111) and of Au(solid) to Pt(111) can be calculated. This is done using Eq. 3.1 derived from Ref. ⁴² which is provided here for reference:

$$n \sum_n \Delta H_{\text{ads}} = -n\Delta H_{\text{sub}} + A[(1 + f)\gamma_{\text{v/m}} - E_{\text{adh}}] \quad (7.6)$$

where $\gamma_{\text{v/m}}$ is the surface energy of the bulk solid (the surface energy of the 111 surface of Cu or Au), f is the surface roughness factor ($f = 1$ for a continuous overlayer as is the case here, compared to 2 for hemispherical cap shaped nanoparticles), $\sum_n \Delta H_{\text{ads}}$ is the integral (average) molar heat of adsorption up to some multilayer coverage, n is the number of moles of the adsorbate on the surface at that coverage, A is the total area covered by admetal film, and ΔH_{sub} is the bulk heat of sublimation of the bulk admetal(solid).

For Cu, the adhesion energy determined in this way is 3.78 J/m^2 at 3 ML and above. (Small inaccuracies in absolute heat calibration make results at 5 ML and above less reliable, so only the values found at 3 and 4 ML are presented, both 3.78 J/m^2 .) This adhesion energy of Cu on Pt(111) is slightly stronger than the adhesion of two Cu(111) planes in bulk Cu(solid), which is equal to two times the surface energy ($2 \times 1.79 = 3.58 \text{ J/m}^2$).⁴² This result explains the driving force for Cu to form a continuous film on Pt(111).⁴² For Au on Pt(111), the adhesion energy (3.74 J/m^2 at 3 ML and above) is nearly the same value as found for Cu, and is also larger than two times the surface energy of Au(111) ($2 \times 1.51 = 3.02 \text{ J/m}^2$),¹⁴⁹ again explaining the formation of Au layers rather than 3D particles. However, it should be noted that the surface energy of Au(111) is substantially lower than the surface energy of Cu(111), therefore despite the fact that the adhesion energy values

for Cu and Au layers to Pt(111) are similar, the *difference* between the adhesion energy and the adhesion of two (111) planes in the bulk metal(solid) is larger for Au than for Cu.

7.4 DISCUSSION

7.4.1 The Growth and Adsorption Energetics of Cu Layers on Pt(111)

The growth Cu overlayers on Pt(111) have been extensively described in literature^{325–328} and summarized above. These literature results are used to analyze the shape our heat curve in Figures 1 and 2. STM by Holst et al.³²⁵ has shown that pseudomorphic Cu islands in the first monolayer nucleate at Pt step edges and then grow outward onto terraces in a tendrill pattern via step flow growth.³³⁶ We therefore assign the initial heat of adsorption of 357 kJ/mol to Cu adsorbing primarily as small 2D islands attached to Pt step edges. This heat is larger than the energy Cu-Cu bonds in bulk Cu(solid) (337 kJ/mol), indicating Cu-Pt bonds are stronger than Cu-Cu bonds. As the Cu islands grow in the first monolayer and Pt step edges become titrated, a smaller fraction of incoming Cu atoms can bond to Pt step edges. As a result, the Cu heat of adsorption decreases in the first monolayer. If the fraction of Cu-Cu compared to Cu-Pt bonds formed in each calorimetry pulse were the only factor that determined the heat of adsorption in region 1, then we would expect the heats in this region to become constant after all of the Pt step edges were titrated, which is not the case. Therefore, we ascribe the linear decrease in heat of adsorption within the first layer to lattice strain caused by pseudomorphic growth.

Figure 7.5 illustrates an idealized situation where a 2D Cu(111) island lies flat on a Pt(111) surface and both the Pt and Cu have their ideal (111) lattice spacing. The central Cu atom in the island is aligned to sit in its most favorable adsorption site on Pt(111), furthest down one well of the periodic potential shown (shown in the bottom of Figure 7.5), which represents the potential energy versus distance for an isolated Cu adatom. As the island size increases (beyond this one

atom), the Cu atoms are displaced out of the ideal binding site due to an 8% lattice mismatch with Pt(111). As a result, the Cu atoms sit higher and higher up the potential energy curve, i.e. in increasingly energetically less favorable sites than the initial Cu atom. As discussed previously, Cu grows pseudomorphically in the first layer, adopting approximately the Pt(111) lattice spacing, so that all Cu atoms sit in the most favorable adsorption site. However, this alignment comes at an energy penalty of increasing the length of Cu-Cu bonds, which are energetically less favorable than those of bulk Cu(solid), causing a decrease in the heat of adsorption in region 1. Because this strain induced in the Pt layer acts in opposite directions on neighboring Cu islands (inwards towards the center of the islands), the Cu islands will repel each other as they grow closer.⁷⁸ This strain presents an additional energy penalty that will cause further decrease in the heat of adsorption.

The heat of adsorption ultimately becomes equal to the bulk heat of sublimation of Cu(solid) at multilayer coverage as expected, but in region 2 (i.e., where most of the Cu adds to the 2nd Cu layer), it is lower than this value by 1 to 4 kJ/mol. We attribute this lower heat in layer 2 to the much stronger bonding of Cu to Pt in layer 1. Stronger bonding in layer 1 means that the Cu in layer 1 has a lower chemical potential than Cu in the bulk. Consequently, it cannot bond as aggressively to the next Cu layer, since lower “chemical potential” means what that name implies: less chemical bonding capacity to the next neighbor that approaches it.⁵⁶

An alternative explanation of this lower heat of adsorption may be explained by the appearance of new LEED spots in the second Cu layer with the Cu(111) spacing, as described above.³²⁶ As this second layer grows, it forms bonds with the first Cu layer below it that has the non-ideal spacing of Pt(111), therefore half of the Cu-Cu bonds formed by the second layer are with strained Cu atoms in the first layer, making the adsorption energy of Cu in this second layer

lower than it would be on a bulk-like Cu film. This lower heat extends slightly above 2 ML coverage, which we attribute to Cu atoms that randomly land on layer 2 islands and populate layer 3 (which is more stable than layer 2) before layer 2 completes, thus leaving sites in layer 2 available beyond 2 ML. This broadens the transition from layer 2 heats to the higher heats in layer 3 and beyond, as observed.

A similar broadening happens in the transition from layer 1 to layer 2 heats. Paffett et al.³²⁶ saw CO uptake up to 1.2 ML Cu on Pt(111), indicating holes in the first Cu layer may still be present after 1 ML. The initial decrease in heat just beyond 1 ML is therefore attributed to a small fraction of Cu atoms filling in the remainder of the first Cu layer, which would form more energetically favorable Cu-Pt bonds. Additionally, as mentioned previously, Paffett et al.³²⁶ observed new Cu (1 x 1) LEED spots at ≈ 1.6 ML, indicating layer 2 has a lattice parameter very close to that of Cu(111). However, Miszczuk et al.,³²⁷ who grew their films at 330 K, did not see the ideal Cu(111) spacing until 5 ML Cu. It is unlikely that the Cu films are perfectly ordered above 3 ML, but the lattice strain is sufficiently relaxed to not affect the heat of adsorption.

7.4.2 The Growth and Adsorption Energetics of Au Layers on Pt(111)

Although the two different mechanisms of growth for Au and Cu seem similar, the shape of their adsorption curves is markedly different. To understand this difference, we turn to an evaluation of the literature on the growth of Au layers on Pt(111).

The larger value of the initial heat of adsorption of Au onto Pt(111) is consistent with the larger value of the heat of sublimation of Au(bulk), which represents the stronger ability of Au to form bonds. The initial sharp rise in the energy 0 - 0.03 ML in region 1, as seen in Figure 7.3 (and more closely in Figure 7.4), is attributed to particle-size effects. In other words, clusters that are smaller than a trimer form on Pt(111) step edges, and these Au adatoms acquire additional metal-

metal bonds as they form dimers and trimers. This situation results in an increase in the heat of adsorption until all adatoms have formed trimers and optimized the number of Au-Pt bonds at steps plus Au-Au bonds. Observations consistent with this scenario have been noted previously for the growth of 3D-particles,^{35,39} where Au forms 2D-islands because of the strong binding to the underlying Pt. Therefore, the initial high heat of adsorption measured here of 382 kJ/mol (which is larger than the heat of sublimation of bulk Au(solid)), and subsequent sharp rise in heat to 393 kJ/mol are attributed to small 2D-clusters of Au growing at Pt step edges.

In the region from 0.03 - 0.7 ML, the Pt step sites have been titrated and the islands continue to grow by Au adatoms binding to the corner of an existing Au island, where they form the maximum number of bonds to other Au atoms in the island (three) plus bonds to the Pt atoms in the layer beneath. In other words, the observed constant heat of adsorption at 393 kJ/mol represents the continuous addition of Au atoms to the corners of 2D islands. This scenario is similar to the case of Cu adsorption, however, in the case of Au, the fraction of Au-Au compared to Au-Pt bonds formed in each calorimetry pulse is the only factor affecting the heats from 0.03-0.7 ML, and the heats remain constant after all of the Pt step edges are titrated, as predicted above when lattice strain is not extracting an energy penalty in this region.

Au is larger than Cu, and more similar in size to Pt. The mismatch between Au(111) and Pt(111) is only 4%, compared to the 8% between Cu(111) and Pt(111). This difference appears to be enough to prolong the linear drop in energy until 0.7 ML, and the heats of adsorption remain approximately constant. From 0.7 - 1 ML, this smaller mismatch and the resulting island-island repulsion that it generates (see above) is enough to produce a linear decrease in the heats of adsorption down to the value of the heat of sublimation of bulk Au(solid). It is possible that at low coverage, the expanding 2D Au islands retain a higher degree of mobility than small Cu islands,

allowing them to maximize their spacing. However, at higher coverage these islands must coalesce, resulting in a doubling of their average size. As described above, the associated energy penalty is proportional to the average diameter of the island. Additionally, initial-island growth may either begin at an HCP or FCC hollow site, and when the islands begin to overlap, this results in high-energy grain boundaries.

Another difference between the Au and the Cu heat of adsorption curves is found in the second and third layers. Rather than being slightly lower than the bulk heat of sublimation of Au(solid), the heat of adsorption is slightly *larger*. For Cu, it was proposed that the decrease in the heats of adsorption in the second layer was due to its lower chemical potential caused by strong binding to Pt. Au similarly binds more strongly to Pt than to itself but does not experience this dip. Rather, this difference is likely further evidence of the second effect described above, where the dip is caused by the adoption of the ideal Cu(111) lattice spacing by the second layer. If, as indicated by LEED,³¹³ Au layers can readily contract to obtain the Pt(111) spacing with a minimal energy penalty, and then gradually and continuously relax into their ideal bulk Au spacing, then this explains why a lower adsorption energy effect is not seen for Au. Instead, what is observed instead is a repeat of the pattern of the growth of the first layer, but with decreasing effects from the underlying, strong-binding Pt that can still be “felt” by adsorbing Au atoms. By region 3 (3-5 ML) as with Cu, the Au films become thick enough that the heat of adsorption reaches the bulk heat of sublimation of Au(s), and the Au gradually relaxes to the Au bulk lattice parameter.

In addition to the smaller difference in atomic size, there is another physical effect that is unique to Au that explains why Au does not suffer the same energy penalty as Cu when forming the first layer. When bulk metals terminate at a low-index surface, the lattice spacing typically contracts at room temperature. This contraction is especially strong for the Au(111) surface, and

it is the only (111) metal surface that undergoes a reconstruction at room temperature (forming a Herringbone reconstruction).^{337,338} Therefore, while there exists a 4% mismatch between the Au and Pt bulk lattice constants, this strong observed contraction of the Au(111) may be enough to offset the strain effects induced by the 4% smaller lattice parameter of Pt, which likely contributes to the stability of the pseudomorphic growth. This is further supported by the LEED spots that show a much more gradual relaxation to the ideal Au(111) spacing. Therefore, it can be concluded that physical, morphological effects such as size and lattice spacing are the primary properties that contribute to the notable difference in the shapes of the heats of adsorption curves vs coverage for Au and Cu on Pt(111).

7.4.3 Comparison to Cu Energetics From Different Methods

Previous work by Cadle et al.³³⁹ and Leung et al.³⁴⁰ measured the difference in binding energy of the first Cu layer on polycrystalline Pt and Pt(111) compared to all other layers using underpotential deposition respectively. In underpotential deposition, Cu is electrochemically removed from a Pt electrode. The voltage difference necessary to remove the outer Cu layers and the first Cu layer can be used to calculate the difference in binding energy of these layers. Cu was observed to bind 39 kJ/mol more strongly to a polycrystalline Pt electrode than itself (i.e., compared to the bulk heat of Cu sublimation),³²⁶ which would correspond to a heat of adsorption of 376 kJ/mol (heat of Cu(bulk) sublimation plus the measured electrochemical difference) and 83 kJ/mol more strongly to Pt(111) than itself.³⁴⁰ This number (376 kJ/mol) is the average heat of adsorption of all Cu atoms in the first monolayer (in the presence of solvent). To compare this value to our heat of adsorption data in Figure 7.1, the integral (average) heat of adsorption in region 1 is calculated, which is 349 kJ/mol, and lower than that observed for electrochemical deposition

on both types of Pt electrodes. The increased heat of adsorption in underpotential deposition can be attributed to solvent effects.

The measured adsorption energies here are important benchmarks to test the accuracy of theoretical calculations. To our knowledge the only DFT calculation of the adsorption energy of Cu onto Pt(111) has been done by Pašti et al.³¹⁴ using the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) approximation. The adsorption energies were determined for 5 different coverages ranging from 0.25 to 1 ML, and corrected for the difference between energy and enthalpy by adding 0.8 kJ/mol (RT) to compare to our calorimetric heats of adsorption measurements in Figure 7.1 and Figure 7.2. The DFT calculations of Pašti et al.³¹⁴ estimated the integral heat of adsorption to be 338 kJ/mol at 0.25 ML (which is a Cu single atom based on the (2 x 2) unit cell used in the calculations), increasing to 377 kJ/mol by 1 ML. This value at 1 ML can be compared to our integral heat of adsorption at 1 ML of 349 kJ/mol from Figures. 1-2. The increased heat of adsorption with coverage in this DFT calculation is due to the increasing Cu-Cu lateral attractions in Cu islands, also seen in calculations of a free-standing Cu layer. Results in Figure 7.1 and Figure 7.2 show that the heat of adsorption of Cu versus coverage behaves opposite of this prediction by DFT, decreasing with increasing Cu coverage. The failure of DFT to correctly predict the measured results is because DFT assumes a structure at 1/4 ML that is incorrect, with the Cu in a 2 x 2 overlayer rather than in 1 x 1 islands as observed.

7.5 CONCLUSIONS

Using single-crystal adsorption calorimetry, Cu was found to adsorb onto Pt(111) with an initial heat of adsorption of 358 kJ/mol, and to decrease linearly in the first monolayer, which was well fit by the equation, $\Delta H_{\text{ads}} = (358 - 19\theta)$ kJ/mol. Cu grows layer-by-layer on Pt(111),

forming misfit layers at room temperature. The observed decrease was explained by fewer Pt-Cu bonds, which are stronger than Cu-Cu bonds, being formed as total Cu coverage increased, and lattice strain in the topmost Pt and Cu layers due to lattice mismatch between the (111) crystal faces of these two metals. The lattice strain caused the Cu heat of adsorption between 1 and 3 ML was lower than Cu(metal) heat of sublimation. After 3 ML the Cu heat of adsorption reached Cu(metal) heat of sublimation. Comparatively, Au was found to adsorb onto Pt(111) with an initial heat of 382 kJ/mol and increase sharply to 393 kJ/mol by 0.03 ML, where it remains approximately constant until 0.7 ML, and then decreases linearly to the bulk heat of sublimation of Au(s) (368 kJ/mol¹⁸). This pattern of rise-level-fall is repeated from 1 - 2 ML and 2 - 3 ML, but the constant adsorption energy value is smaller, at ≈ 374 kJ/mol and ≈ 371 kJ/mol respectively. After 3 ML the Au heat of adsorption reached Au(metal) heat of sublimation. The adhesion energy of the first ML of Cu to Pt(111) at 300 K was determined to be 3.84 J/m^2 and decreased to 3.76 J/m^2 by 4 ML. The adhesion energy of the first Au layer was found to be 3.57 J/m^2 , and increased to 3.74 J/m^2 by 4 ML. These results are important benchmarks for testing the accuracy of quantum mechanical calculations of metal/metal bonding such as in density functional theory.

7.6 FIGURES

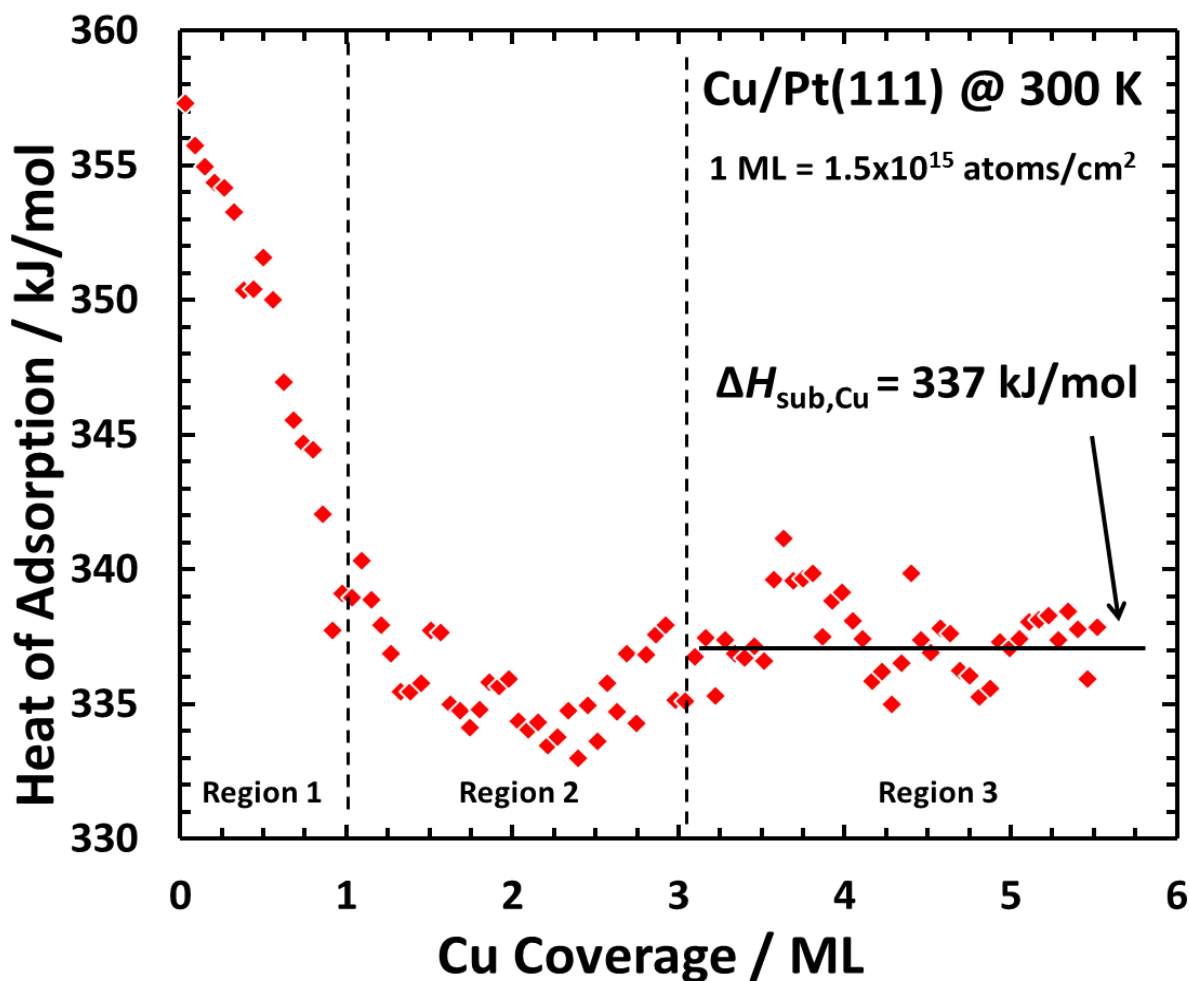


Figure 7.1. Heat of adsorption of Cu atoms onto clean Pt(111) (average of 3 experiments) at 300 K versus Cu coverage. The data are discussed in terms of three distinct regions of coverage. In Region 1 (0-1 ML), 2D Cu islands grow pseudomorphically on Pt(111); in Region 2 (1-3 ML) a large fraction of the Cu film is 2 layers thick; and in Region 3 (>3 ML), bulk-like Cu(111) grows in islands that are at least 3 layers thick.

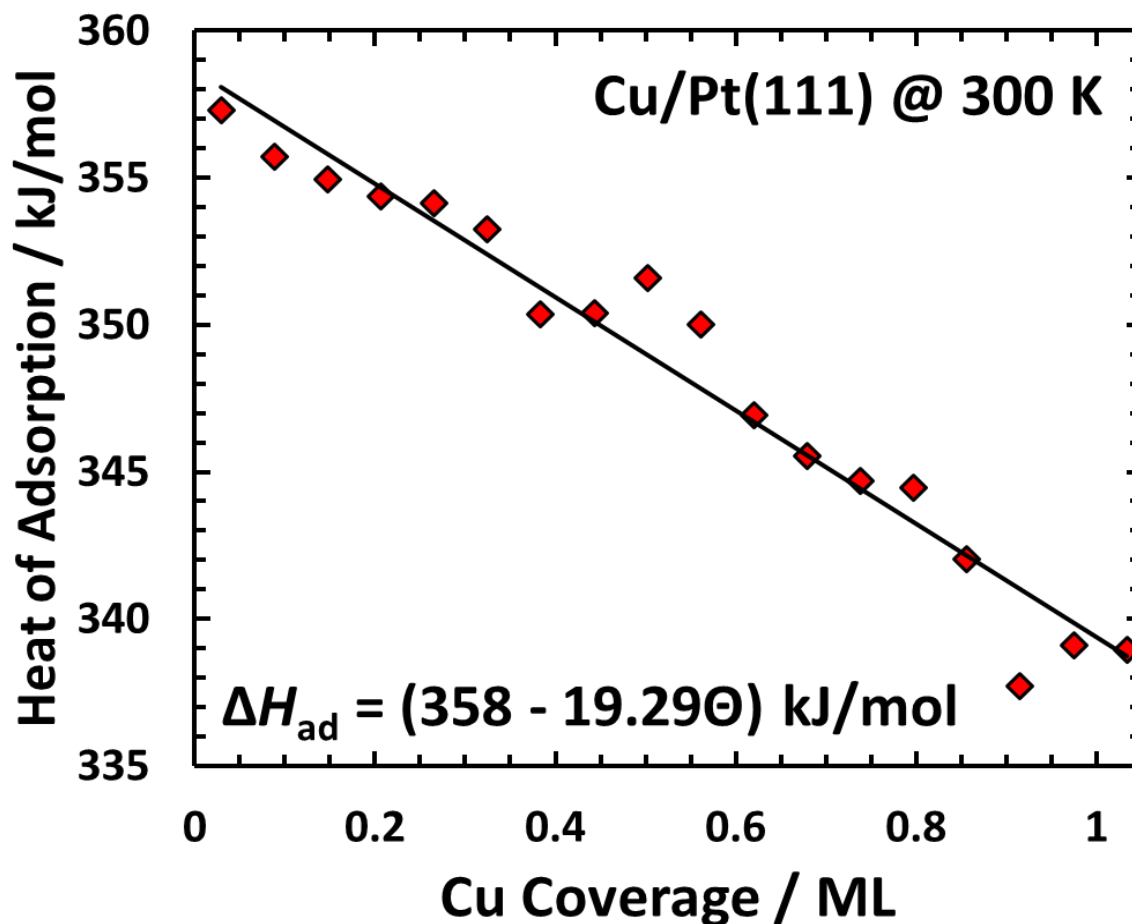


Figure 7.2. The Cu heat of adsorption in the first ML on Pt(111) from Figure 7.1. Despite Cu islanding (attractive Cu-Cu interaction), a decrease in the heat of adsorption is observed due to lattice strain in the first Pt(111) layer and Cu overlayer, associated with the 8% lattice mismatch between bulk Cu(111) and Pt(111). The data from Region 1 is well fit as a linear decrease in heat of adsorption with Cu coverage as shown.

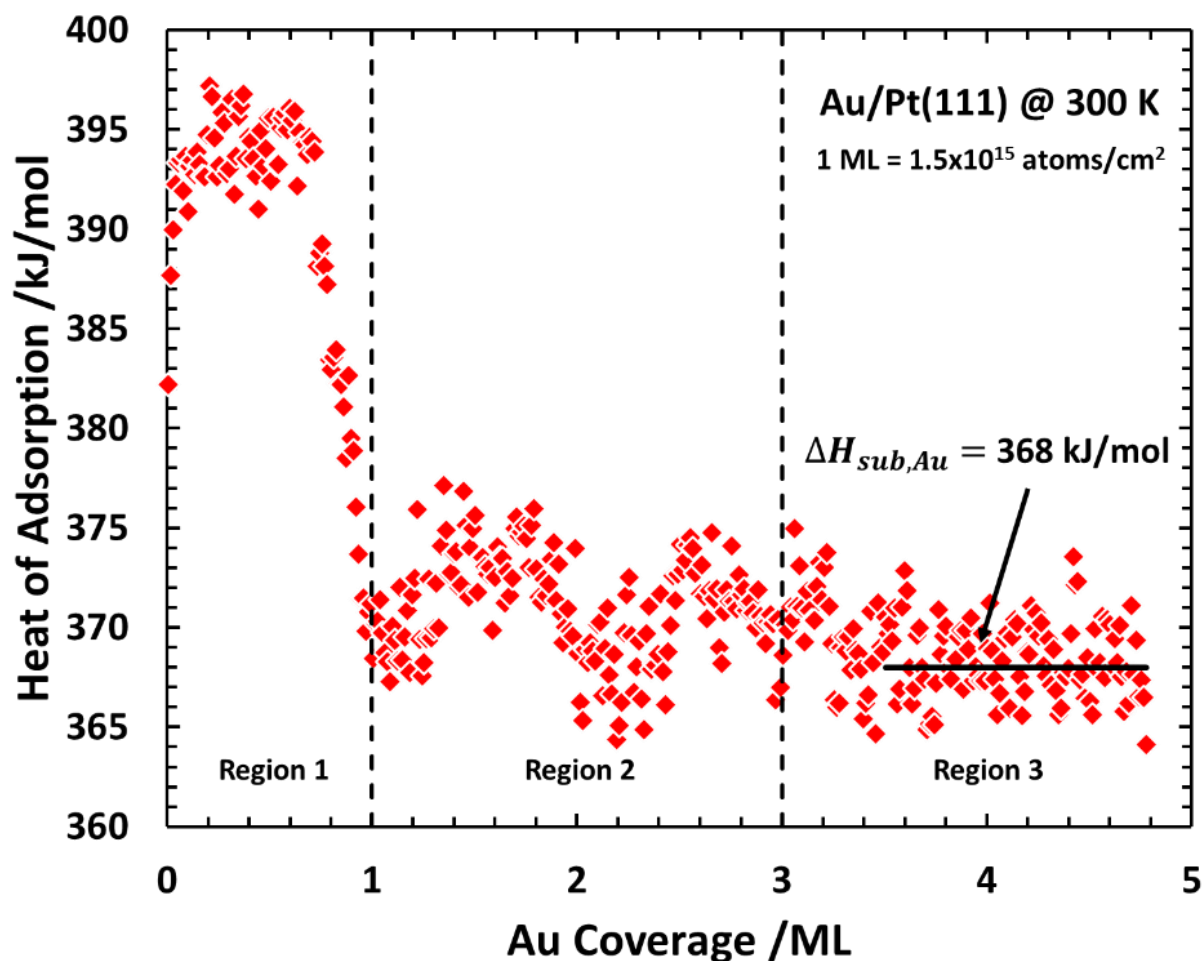


Figure 7.3. Heat of adsorption of Au on clean Pt(111) surface (average of 3 experiments) at 300 K as a function of Au coverage. The heat data is divided into 3 distinct regions of Au coverage: Region 1 (0 – 1 ML) where 2D-islands of Au grow pseudomorphically with the Pt(111) substrate; Region 2 (1 - 3 ML) where the second and third monolayer grow with a heat that is slightly higher on average than the bulk heat of sublimation, and Region 3 (3 ML and above) where layers grow with a heat of adsorption equal to the bulk heat of sublimation of Au(s).

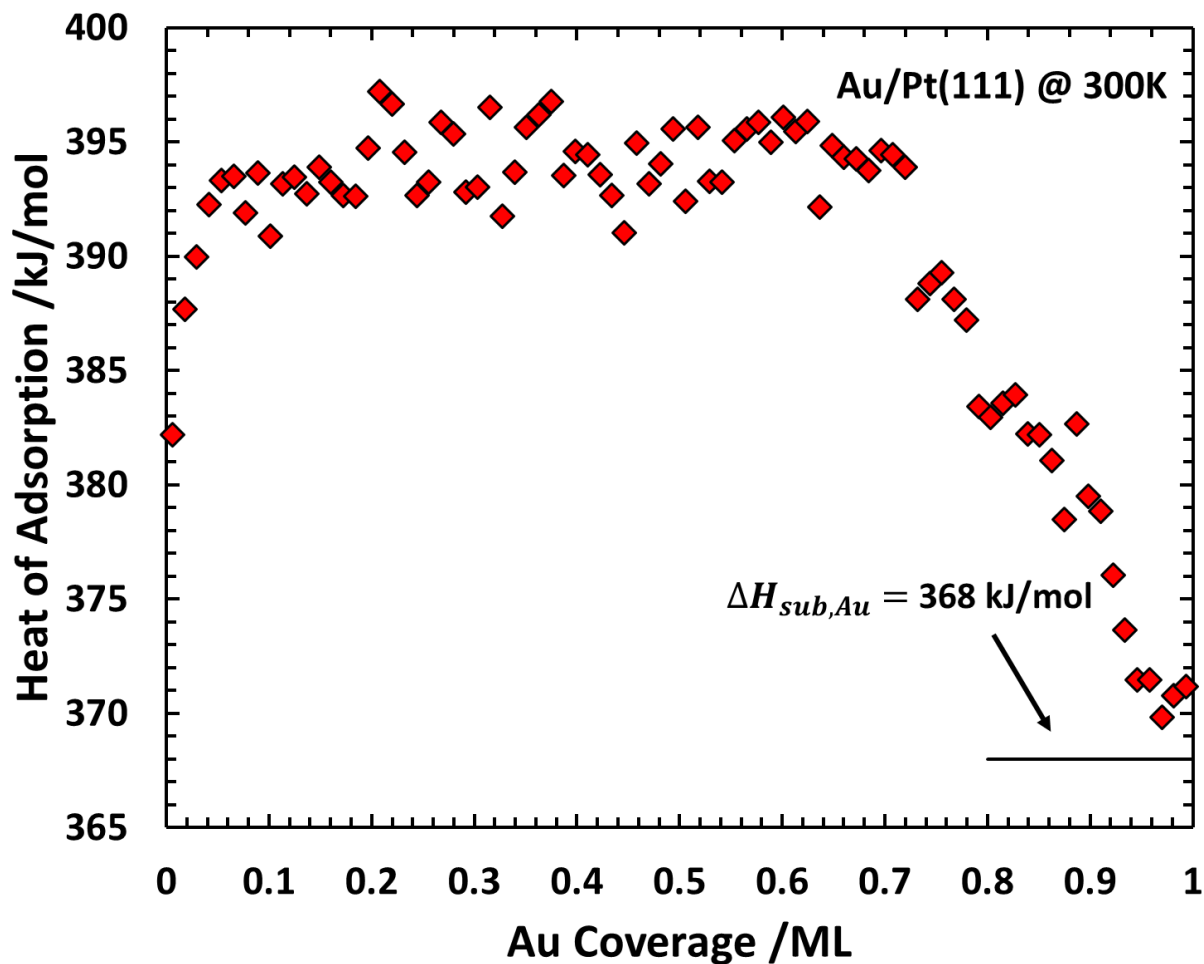


Figure 7.4. The heat of adsorption versus coverage in the first ML of Au on Pt(111) from Figure 7.3. At very low coverage, 2D particle-size effects result in an increasing heat as monomers and/or dimers form additional metal-metal bonds as the cluster size grown. From 0.03 - 0.7 ML the energy remains nearly constant as the relative number of Au-Au bounds and Au-Pt bonds formed is fixed because new Au atoms are incorporated at edge of island in kink sites. Above 0.7 ML the 2D-islands begin to merge, exacting increasing larger energy penalty due to slight lattice mismatch.

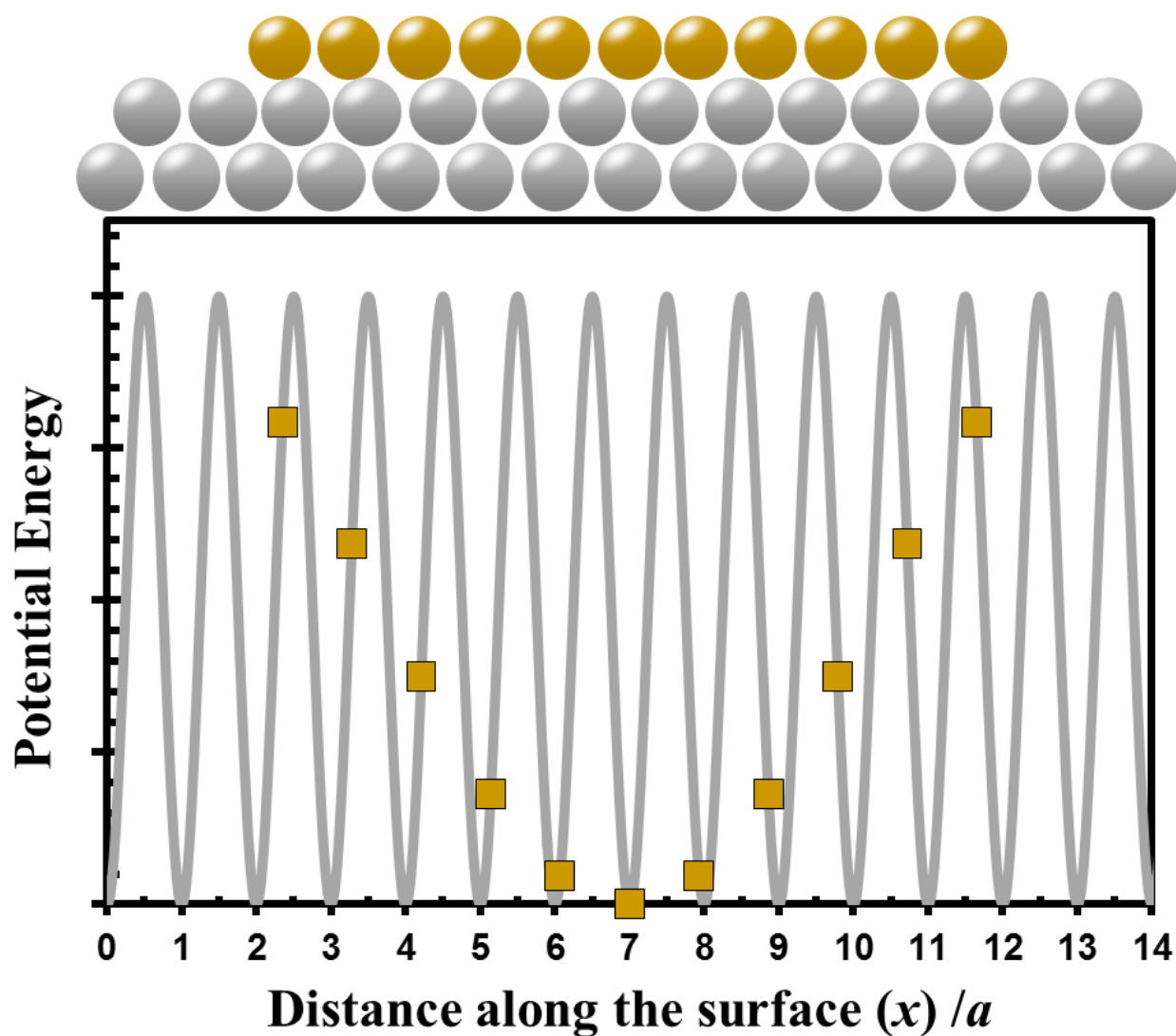


Figure 7.5. Schematic illustration of the energetics of adsorbed Cu atoms for small 2D Cu island growth on the Pt(111) surface, showing a hypothetical situation (not observed) where Cu does not adopt pseudomorphic growth, but instead grows with a bulk-like Cu(111) lattice spacing. Note that this scenario would cause Cu to sit in increasingly stable adsorption sites as the Cu island size grows. If the Pt atoms in the top layer moved slightly toward the island center, and if the Cu atoms near the edges of the islands moved outward from the island center, the energy for the Cu atoms near the edges of the island would decrease. This movement gives rise to forces that increase with island size (i.e., with coverage for a fixed number density of 2D islands), so the lattice strain grows with island size. The decrease in heat of adsorption with coverage in the 1st monolayer is attributed to this island-size effect.

Chapter 8. Preparation of Fe₃O₄(100) Films and the Adsorption of Water by SCAC

This chapter contains unpublished results

This work was conducted at the Fritz Haber Institute in Berlin, Germany, and is detailed here
with permission from the authors:

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In this chapter, a single-crystal adsorption calorimeter located at the Fritz Haber Institute in Berlin, Germany was used to characterize the interaction of water with a well-defined epitaxial Fe₃O₄(100) / Pt(100) substrate. At 120 K, initial adsorption energy was found to be 67 ± 1 kJ/mol, which is $\approx 30\%$ lower than the corresponding value found on Fe₃O₄(111)³⁴¹. Temperature-dependent sticking probability measurements indicate further that the (100) surface of magnetite is less reactive than the (111) surface. The structure-activity relationship is discussed in terms of the Lewis acid properties of the coordinatively unsaturated cation sites present at the oxide surfaces.

8.1 INTRODUCTION

Surface properties of magnetite Fe₃O₄ have been attracting considerable attention both in catalysis and in materials science research.^{342–344} This naturally occurring oxide has been found to be reactive towards several small molecules and key catalytic intermediates (such as CO₂ and

water), and consequently has the potential to be utilized as a cheap heterogeneous catalyst.^{345–349} Indeed, iron oxide-based catalysts are already used in production of styrene, and in the production of hydrogen via the water-gas shift reaction (WGSR).^{350,351} The latter process is of special technological significance because of its application in large-scale industries such as ammonia synthesis (for agricultural fertilizers) and methanol synthesis (for fuel cell applications).³⁵²

There are two primary reaction mechanisms that are considered to underlie the heterogeneously catalyzed WGSR.^{351,352} In the associative mechanism, adsorbed water and CO form intermediate surface complexes that essentially follow Langmuir–Hinshelwood kinetics. Alternatively, the so-called redox mechanism refers to the Mars-van Krevelen reaction type where the oxide surface is alternately reduced by CO and oxidized by H₂O. For both pathways, the adsorption of water and its interaction with the surface represents an important elementary step, and it is commonly believed that the WGSR is driven by surface hydroxyls groups formed by dissociated water molecules.³⁵³

Although the interaction of water with the most abundant (111) and (100) magnetite surfaces has been extensively addressed by various surface sensitive techniques, the data available are somewhat contradictory, particularly in terms of the relative reactivity of the two surface terminations. For example, photoelectron spectroscopy measurements of water adsorption on bulk-like Fe₃O₄ single crystals indicated that hydroxylation of both the (111) and (100) surfaces is accelerated by increasing water exposure, which leads to a strong pressure dependence.^{354–356} However, UHV studies on epitaxially grown Fe₃O₄(111) films revealed instant water dissociation followed by molecular adsorption of water upon the completion of one monolayer.^{357,358} These findings were recently addressed by molecular beam experiments on Fe₃O₄(111) films and DFT calculations³⁴¹ In this study, the surface chemistry of water on Fe₃O₄(111) was shown to be facile,

and to yield a dimer species on the surface (a water-hydroxyl complex). However, there is extensive evidence in the literature that water chemisorbs on $\text{Fe}_3\text{O}_4(100)$ under UHV conditions for both thin film and bulk samples.^{347,359}

In this Chapter, single-crystal adsorption calorimetry (SCAC) measurements of water adsorption on an epitaxially grown $\text{Fe}_3\text{O}_4(100)$ / $\text{Pt}(100)$ film are presented and compared to previous data reported for $\text{Fe}_3\text{O}_4(111)$ acquired using the same technique in the same UHV chamber.³⁴¹ SCAC is extremely valuable as a comparative tool for systems such as this because of its unique ability to directly measure the enthalpy released upon the adsorption and reaction of water with the magnetite surface as a function of total surface coverage and temperature. Consequently, SCAC enables measurements of different species such as molecularly adsorbed water versus hydroxyls.⁹⁴ In this Chapter, the structure-reactivity relationships of the 111 and 100 magnetite surfaces are rationalized on the basis of existing surface models, including the recently upgraded structure of $\text{Fe}_3\text{O}_4(100)$.³⁶⁰

8.2 EXPERIMENTAL DETAILS

The instrument used for this experiment is similar to the one described in Chapter 2, and is housed at the Fritz Haber Institute in Berlin, Germany. A detailed account of the operation of this two-chamber UHV apparatus has been detailed previously.³⁶¹ A summary of the sections of that account that are relevant to this experiment is presented here.

$\text{Fe}_3\text{O}_4(100)$ films were prepared by physical vapor deposition on 1 μm thick $\text{Pt}(100)$ samples obtained from Jacques Chevallier at Aarhus University. The growth recipe was originally developed by Davis et al.³⁶² for ≈ 1 mm thick $\text{Pt}(100)$ crystals, and was reproduced for the thinner substrate. The $\text{Pt}(100)$ crystals were cleaned by successive cycles of 1 kV Ar^+ sputtering in 4×10^{-6} Torr Ar followed by annealing to 1200 K in UHV for five minutes. A 3 nm thick Fe

(99.995, Alfa Aesar) metallic buffer layer was deposited with an e-beam evaporator in UHV at a deposition rate of ≈ 1 Å/min for 30 minutes. The deposition rate was calibrated using a translatable QCM that was placed at the sample position. Following deposition of the buffer layer, Fe was deposited at the same rate, but in 7.5×10^{-5} Torr O₂ for 30 minutes to form the oxide layer. Following oxide deposition, the film was annealed in three success steps, the first for 20 minutes in UHV at 880 K, the second for 20 minutes in UHV at 1080 K, and the third for for 5 minutes in 3.7×10^{-7} Torr O₂.

As with the instrument described in Chapter 2.5, the absolute calibration of the heat detector response is obtained by measuring a 623.8 nm HeNe laser pulse of known power that impinges on the sample. The fraction of the incoming laser light that is absorbed by the sample is based on the sample's reflectivity. While this value is known for most bulk metals, the reflectivity of thin oxide films can vary with thickness. For metal adsorption, if there is an error in the presumed reflectivity, the final calibration can be scaled by the known heat of sublimation of the metal. However, for molecular adsorption, the heat of the steady-state on a surface is not well-known, therefore, the reflectivity must be measured directly in UHV conditions.

This measurement was achieved with a reflectivity measurement setup located in the preparation chamber, which is detailed in Figure 8.1 (reproduced with permission from Reference ³⁶¹) In brief, a 632.8 nm He–Ne laser (1) similar to the one used for calorimetry calibration is mounted in front of a window (2) that points toward the center of the chamber where the manipulator is located. The manipulator holds a thick (1 mm) Pt(100) sample and five dielectric mirrors of known reflectance. The laser light passes through a linear polarizer (7), and is split by a polarization-dependent beam splitter (5). One portion of the laser light is detected by the sampler photodiode (6), and the other passes through the window and impinges on the sample or the mirror

surface at an angle of $\approx 5^\circ$ relative to the surface normal. The reflected intensity is then measured by the main photodiode (4) placed next to the laser. The ratio of the intensities at the two photodiodes $I_{\text{main}}/I_{\text{sampler}}$ is directly proportional to the reflectivity of the sample. The mirrors are used as calibration references, and once a proportionality factor is determined, this value is used to measure the reflectivity of an oxide sample grown on the thick Pt(100). This measurement was conducted for ten as-grown 6 nm thick $\text{Fe}_3\text{O}_4(100)$ films, which were prepared as described above on thick Pt(100). The average value of these ten runs was then used as the reflectivity of the 6 nm thick oxide film that was grown on the thin (1 μm) Pt(100). The reflectivity of the thin sample could not be directly measured because the crystal was not guaranteed to be optically flat when it was that thin.

Adsorption of experiments were conducted by dosing D_2O (Deuterium oxide, min. 99.96% D, Sigma-Aldrich) with an effusive multi-channel array source held at room temperature onto oxide films grown on the thin Pt(100) crystal.^{361,363,364} The backing pressure of the effusive source was ≈ 1 mbar, which gave an approximate flux of 3×10^{13} D_2O molecules per pulse, with pulse lengths of approximately 266 ms. A five second delay between D_2O pulses was used to avoid any overlap between adsorption and subsequent reaction or desorption. The flux of the beam was measured using a liquid nitrogen cool quartz crystal microbalance (QCM).

The heat released per pulse of D_2O was measured with a pyroelectric heat detector similar to the one described in Chapter 2.4, but oriented at 90 degrees relative to the setup above. The sample holder and detector can be cooled to temperatures from 120 – 300 K. The reference signal for the sticking probability (achieved by the King–Wells method⁸⁹) uses a gold flag (rather than a heated Ta flag) positioned between the sample and the outer molecular beam aperture. All other details of the sticking measurement are similar to those described in the metal adsorption

experiments, with the QMS set at mass 20. The heats were scaled by the measured short-term sticking probability, and the long-term sticking probability was used to scale the total coverage (described below). A rotatable platform holds a beam-flux monitor (which operates on the principle of an accumulation detector^{361,363}), a photodiode, and the sample, which can each be placed 4 mm from the opening of the molecular beam.

8.3 RESULTS

8.3.1 Fe₃O₄(100) Film Growth

After cleaning, the Pt(100) crystals exhibit the characteristic hex-reconstruction pattern in LEED (Figure 8.2a). Depositing an Fe buffer layer lifts the hex-reconstruction of the Pt(100), resulting in a diffuse (1 x 1) LEED pattern from an epitaxially grown Fe(001) layer (Figure 8.2b). After oxide growth, the ($\sqrt{2} \times \sqrt{2}$)R45° reconstruction is visible in LEED, but it is diffuse, indicating poor surface order (Figure 8.2c). After annealing, the LEED pattern is sharp, indicating a high degree of surface order (Figure 8.2d). The STM results of Davis et al.³⁶² reveal that this growth procedure produces the most stable “B-layer” terminated surface, which consists of octahedrally coordinated iron and tetrahedrally coordinated oxygen, with one subsurface oxygen vacancy per unit cell.³⁶⁵ This configuration is stabilized by Jahn-Teller distortion with a wavelike displacement of Fe and O atoms in the top B layer.^{366,367} A cartoon of this surface is shown in Figure 8.3. During adaptation of the growth from the STM chamber to the calorimetry chamber, it was determined that the order according to LEED was similar for buffer and oxide layer thicknesses of 2, 3, and 4 nm. A total of 6 nm thick films were used (3 nm buffer layer, 3 nm oxide layer) to replicate the conditions of similar experiments conducted on the Fe₃O₄(111) surface.³⁴¹

8.3.2 In Situ Oxide Film Reflectivity Measurements

The mirrors used for the calibration procedure described above have known reflectivities of $41.4 \pm 0.4\%$, $59.7 \pm 0.9\%$, $76.7 \pm 1.1\%$, $86.2 \pm 0.2\%$, and $96.6 \pm 0.1\%$. Figure 8.4 shows the reflectivity of the five mirrors at 632 nm plotted as a function of the measured ratio $I_{\text{main}}/I_{\text{sampler}}$. The slope of the calibration curve was calculated by measuring the laser intensity ratios of each mirror 12 times on 12 different days. The resulting data (open circles) for the calibration mirrors represent the average intensity ratio for each point. The error bars show the standard deviation of these measurements. The slope of the final calibration curve was the average of the 12 slopes from each procedure. This final calibration slope was used to measure the reflectivity of Pt(100) and of five different preparations of 6 nm thick as-grown $\text{Fe}_3\text{O}_4(100)$ films on 1 mm thick Pt(100). This procedure gave a reflectivity of $75.2 \pm 0.3\%$ for Pt(100), and $65.2 \pm 0.4\%$, for 6 nm thick $\text{Fe}_3\text{O}_4(100)$.

8.3.3 Sticking Probability of Water on $\text{Fe}_3\text{O}_4(100)$

In previous chapters, sticking probability per pulse has been discussed as a single quantity, however, it is in fact two different phenomenon that can occur during calorimetry measurements. The short-term sticking probability is the probability that atoms or molecules in the gas phase pulse will stick on the surface for the entire duration of the pulse window. Here the duration is 266 ms, whereas for metals it was 102 ms. A second quantity – the long-time sticking probability – is defined as the probability that atoms or molecules in the gas pulse will stick until the next pulse arrives (which here is 5 seconds later). The long-term sticking probability is used to calculate the total coverage at the start of the next pulse, while the short-time sticking probability is used to calculate adsorption energies per mole adsorbed. Typically for metal adsorption, all the atoms that will desorb do so within the time window of the pulse (meaning that there is no additional

desorption between pulses); metal multilayers can build up on the surface indefinitely, therefore the short-term and long-term sticking probabilities are the same. However, this is not the case for D₂O adsorption on Fe₃O₄(111).

At 120 K, the short-term and the long-term sticking probabilities were the same ($\approx 92\%$), and they remained constant on both Fe₃O₄(100) and the Pt(100) as a function of total water coverage, at which point multilayer ice can form. However, at all higher temperatures, the system reached a saturation coverage of D₂O (which varied by temperature). In this regime, the system is in a dynamic adsorption–desorption equilibrium process, in which adsorption during the molecular beam pulse is equal to the desorption before the next pulse. In other words, the long-term sticking probability drops to zero, while the short-term sticking probability remains at some constant value.

The short-term sticking probability of water was found to be independent of total water coverage (which is similar to what was observed on Fe₃O₄(111)³⁴¹). The short-term sticking probability on Fe₃O₄(100) is shown in Figure 8.5 as a function of substrate temperature. The sticking probability of water as a function of temperature on the 111 surface is also shown for reference.³⁴¹ From this comparison, it can be seen that the sticking probability of D₂O on Fe₃O₄(100) decreases with temperature, while it remains high on Fe₃O₄(111). By 300 K, the sticking probability on the 111 surface is nearly twice as large as on the 100 surface.

8.3.4 Energetics of Water Adsorption on Pt(100) and Fe₃O₄(100)

Figure 8.6 shows the adsorption energy of D₂O on Pt(100) and Fe₃O₄(100) at 120 K as a function of the total number of adsorbed molecules regardless of the particular atomic structure that they take on the surface. Similar to what was observed on Pt(111),³⁴¹ the adsorption energy of water on clean Pt(100) is essentially constant at 42 ± 1 kJ/mol. This behavior is typical of water that is physisorbed on the surface and does not undergo any decomposition.^{341,368} In contrast, the

adsorption energy on $\text{Fe}_3\text{O}_4(100)$ starts high in the low-coverage limit at 67 ± 1 kJ/mol, and then decreases rapidly with increasing water coverage – remaining higher than the water adsorption energies on $\text{Pt}(100)$ – until it levels out at approximately the same heat as water on the $\text{Pt}(100)$ surface at coverages above 1.5×10^{15} molecules/cm². This constant adsorption corresponds to the formation of the second and subsequent water (ice) layers, when the oxide surface is no longer accessible to incoming water molecules. A similar transition is observable on the $\text{Pt}(100)$ substrate at approximately the same coverage, however the transition between monolayer and multilayer is barely distinguishable.

This behavior is qualitatively similar to what was observed for water on $\text{Fe}_3\text{O}_4(111)$. The high initial heats on the oxide at 120 K indicate a stronger chemical reaction with the surface, which does not occur on Pt. In the case of the $\text{Fe}_3\text{O}_4(111)$ surface, by using a combination of isotopically labeled Infrared Adsorption Spectroscopy (IRAS) and DFT, this chemical reaction was determined to be water dissociatively adsorbing to form hydroxyls that form a water-hydroxyl complex.³⁴¹ This was supported in the case of the (111) surface by measuring the adsorption energies at higher temperatures. When the substrate temperature was increased to 180 K and above, the energy of adsorption in the low-coverage limit was higher by nearly 10 kJ/mol. It was proposed that this result arose because the surface reaction of water is kinetically inhibited at 120 K.³⁴¹

Similarly, on the (100) surface, when adsorption experiments were conducted at 180 K, the initial heat of adsorption increases from 67 to 76 ± 2 kJ/mol. At 210 K, the adsorption behavior was the same as at 180 K, however the long-term sticking dropped to zero at an earlier coverage. At 300 K, the initial sticking probability was very low, and the long-term sticking dropped to zero after the first few pulses.

This increase in the initial heat of adsorption from 120 K to higher temperatures is qualitatively similar to what was observed on the (111) surface,³⁴¹ however the initial adsorption energies on the (100) surface are significantly lower than they are on the (111) surface at all temperatures measured by approximately 20 kJ/mol. These heat data reveal that Fe₃O₄(100) has lower affinity to water than Fe₃O₄(111).

8.4 DISCUSSION

Early TPD experiments of water adsorption on epitaxially grown Fe₃O₄(100) films showed three adsorption states in the first layer, which have approximately equal concentrations at saturation. Their desorption maxima appear at 225, 280 and 300 K.³⁶⁹ More recently, the adsorption of water on a Fe₃O₄(100) / Mo(100) substrate was studied with HREELS, LEED and UPS.³⁵⁹ At low temperatures, two coexisting loss peaks at 456 and 420 meV were found, which were assigned to terminal OH bonds and hydrogen-bonded water, respectively. The latter signal was demonstrated to disappear upon heating, indicating desorption of the molecularly adsorbed species. The STM and LEIS study by Diebold and co-workers showed that only adsorbed H atoms exist on Fe₃O₄(100) following water exposure at 300 K.³⁴⁷ These adsorbed H atoms can also be considered as surface hydroxyls involving a lattice oxygen atom. However, the authors found no associated OH groups from water molecules, which is indicative of their efficient removal at room temperature in UHV. From this result, it can be concluded that the chemisorption of water on Fe₃O₄(100) includes the formation of surface hydroxyl groups, which can further react with each other and/or with the oxide lattice.

Surface reactions involving OH groups on Fe₃O₄(100) are likely to be kinetically suppressed at temperatures as low as 120 K. Since the monolayer is saturated at approximately the

same coverage as it is on the inert Pt surface, it can be concluded that no easily-desorbed products are formed. According to the HREELS data, water dissociation on the oxide is also somewhat hindered, i.e. hydroxyl species are most likely accommodated together with intact molecules. This is confirmed by higher adsorption energy observed at elevated temperatures

In order to understand the difference between the relative water adsorption behavior on these two magnetite surfaces, one can refer to their respective atomic structures. Fe_3O_4 has an inverse spinel structure in which oxygen atoms are packed into a FCC sublattice with the interstitial sites occupied by iron. The tetrahedral positions contain Fe^{3+} , whereas the octahedral sites are populated by equal amounts of Fe^{3+} and Fe^{2+} .³⁷⁰ DFT predicts that multiple terminations are possible for both the (111) and the (100) surface.²⁹¹ Previous DFT results on $\text{Fe}_3\text{O}_4(111)$ found that only one structure satisfactorily described the observed properties of adsorbed water, which was referred to as the $\text{Fe}_{\text{oct}2}$ termination.³⁴¹ Recently, an equilibrium atomic structure for the $\text{Fe}_3\text{O}_4(100)$ surface has been revealed using a combined IV-LEED, STM and DFT study by Bliem *et al.*³⁶⁰ The $(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ reconstructed B-termination was found to be stabilized by an ordered array of subsurface cation vacancies (SCV), where two octahedrally coordinated iron cations are missing in the third layer, while one iron atom appears as an interstitial in the second layer.

A comparison between the proposed $\text{Fe}_{\text{oct}2}$ -terminated $\text{Fe}_3\text{O}_4(111)$ surface and SCV-terminated $\text{Fe}_3\text{O}_4(100)$ surface is depicted in Figure 8.8. One can see that both surfaces expose all possible types of the oxide constituents. However, these adsorption sites are not equivalent from a chemical point of view, particularly in terms of their acid-base properties. In principle, the ions existing in the magnetite crystal structure can work both as Brønsted bases (O^{2-} anions) and Lewis acids (Fe^{2+} and Fe^{3+} cations). Since water has a pronounced amphoteric character, its interaction with iron oxide can be considered an acid-base reaction. Whereas the proton affinity of the oxygen

in metal oxides is typically very high,³⁷¹ the electron-acceptor strength of the iron surface sites is likely strongly dependent on the neighboring atomic arrangement.

The $\text{Fe}_{\text{oct}2}$ termination of the (111) surface is a relaxed bulk truncation along the (111) direction by a mix-trigonal layer. It exposes $\frac{1}{4}$ ML of Fe^{3+} in the tetrahedral positions and $\frac{1}{4}$ ML of the octahedral cations over a closed-packed hexagonal oxygen array. Both types of iron atoms also form hexagonal periodic structures with the same ≈ 6 Å unit cell which gives rise to a surface atomic density of $\approx 3.2 \times 10^{14}$ Fe atoms/cm². Correspondingly, the $\text{Fe}_3\text{O}_4(111)$ unit cell contains two different cation sites and four anion sites, one of which is not equivalent to the other three (Figure 8.8). DFT predicted that water on this surface forms one dimer-like species per unit cell, which is described as follows: one water molecule dissociates into an OH group bound to the octahedral iron plus a proton that sits on the neighboring oxygen that is most distant from the cation. A second water molecule is hydrogen-bonded to the hydroxyl, forming a dimer species, but this water molecule has no direct bonds with the oxide surface.³⁴¹ The coordination number of the exposed octahedral iron is 3 – in other words, the iron is threefold coordinatively unsaturated. The iron atoms in the tetrahedral positions have a coordination number of 5, (only undercoordinated by one) and do not participate in the reaction at low coverage. Thus, water reaction with $\text{Fe}_3\text{O}_4(111)$ includes an interaction with these undercoordinated cation sites.

As mentioned above, the recently discovered SCV model of the $\text{Fe}_3\text{O}_4(100)$ surface properly describes the well-established $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction and other characteristics of the oxide surface, e.g. high stability of deposited metal adatoms. In the SCV structure, the top-most atomic array is based on truncation at the B layer along the (111) bulk direction with the modified A layer underneath. The B layer consists of oxygen and the octahedral iron atoms forming distorted rows in the (110) direction (Figure 8.8). The reconstruction was proven to be

caused by cation vacancies in the third layer and interstitial iron atoms appearing in the second layer.³⁶⁰ The A layer is composed only of the tetrahedrally coordinated cations and the interstitials lower its fourfold bulk symmetry producing the $(\sqrt{2} \times \sqrt{2})R45^\circ$ periodicity. The reconstructed unit mesh is $8.4 \times 8.4 \text{ \AA}^2$ in size, and exposes 8 oxygen atoms and 4 octahedral iron atoms with 3 coordinatively saturated tetrahedral cations beneath (including the interstitial). Similar to $\text{Fe}_3\text{O}_4(111)$, the reaction of water with $\text{Fe}_3\text{O}_4(100)$ was proposed to involve the iron atoms in the octahedral positions.³⁴⁷ However, the coordination number of the octahedral cations on the $\text{Fe}_3\text{O}_4(100)$ surface is 5, meaning that these sites are *less* undercoordinated compared to the threefold Fe sites in $\text{Fe}_3\text{O}_4(111)$. This increased number of bonds can create an electronic screening effect, and therefore the electron affinity of the $\text{Fe}_3\text{O}_4(100)$ surface would be less than of the $\text{Fe}_3\text{O}_4(111)$ surface. In other words, $\text{Fe}_3\text{O}_4(100)$ surface has weaker Lewis acidic character than $\text{Fe}_3\text{O}_4(111)$ (and hydroxides are strong electron-donor species). This line of reasoning is consistent with the lower measured heats of adsorption of water on the (100) surface compared to the (111) surface.

Despite the simplicity of this acid-base approach, the importance of the electrophilic character of the surface cation sites is supported by the comparative sticking probabilities on these surfaces. On both magnetite surfaces, the sticking coefficient of water was independent of coverage, which indicates precursor-mediated adsorption, and supports the formation of hydroxyls and hydrogen-bonded complexes. Therefore, the average sticking probability values at different temperatures presented in Figure 8.5 represent the probability of water molecules to be trapped by reactive Fe sites. As shown, these sticking probabilities clearly differ for $\text{Fe}_3\text{O}_4(100)$ and $\text{Fe}_3\text{O}_4(111)$, with a nearly two-fold smaller sticking probability on the (100) surface compared to the (111) surface at room temperature. In contrast to the SCAC measurements, which deal with

the energetic effects of the overall chemical reactions, the sticking coefficients probe only the primary adsorption process. Thus, the observed temperature dependence directly reflects the decreased water affinity of $\text{Fe}_3\text{O}_4(100)$ compared to $\text{Fe}_3\text{O}_4(111)$

This work reveals that water chemistry on magnetite critically depends on the surface plane exposed. The quantitative information obtained using SCAC combined with a qualitative interpretation of the physical and electronic properties of the surface sheds light into the elementary interactions between water and the magnetite surfaces studied here. However, a more detailed understanding of the reaction mechanism is required to understand the driving force of water chemisorption on $\text{Fe}_3\text{O}_4(100)$ and how the adsorbed water differs structurally (if at all) from the water-hydroxyl complexes formed on $\text{Fe}_3\text{O}_4(111)$. Such a detailed investigation requires additional support from IRAS and DFT, which is currently being conducted at the FHI in Berlin.

8.5 CONCLUSIONS

Well-defined thin $\text{Fe}_3\text{O}_4(100)$ films were grown on $\text{Pt}(100)$, and their reflectivity was found to be $65.2 \pm 0.4\%$. In this study, SCAC has been for the first time employed for a comparative chemisorption study on two different surface planes of an oxide material. The differential adsorption energy of water was found to be 67 ± 1 kJ/mol on $\text{Fe}_3\text{O}_4(100)$ films, and 42 ± 1 kJ/mol on $\text{Pt}(100)$ at 120 K. In contrast, water was previously found to have a stronger interaction with $\text{Fe}_3\text{O}_4(111)$ surface with an initial adsorption energy of 87 ± 1 kJ/mol at 120 K. These data demonstrate that the two magnetite surfaces have significantly different reactivity. The lower water affinity observed on $\text{Fe}_3\text{O}_4(100)$ is described in terms of the weaker Lewis acidity of its surface cation sites, which is caused by a smaller degree of coordinative unsaturation. It is noteworthy that on both oxide surfaces, the adsorption energy of water gradually decreases with surface coverage,

which indicates strong lateral interactions in both cases. Typically, these effects are underestimated in traditional desorption-based experiments.

8.6 FIGURES

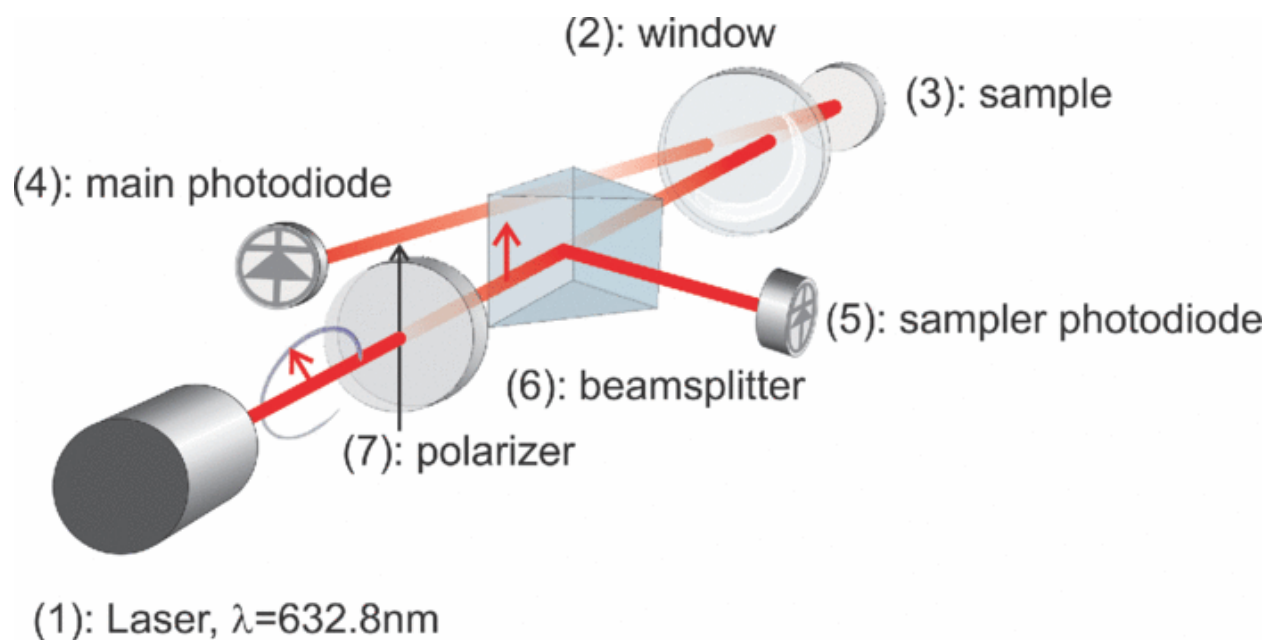


Figure 8.1. Schematic of the setup used for reflectivity measurements, reproduced with permission from Ref. ³⁶¹. The components in this setup are (1) the HeNe laser, (2) the window on the UHV chamber that the laser light shines through, (3) the sample (either the single crystal or the mirrors used for calibration), (4) the main photodiode, (5) the sampler photodiode, (6) the beamsplitter and (7) the linear polarizer.

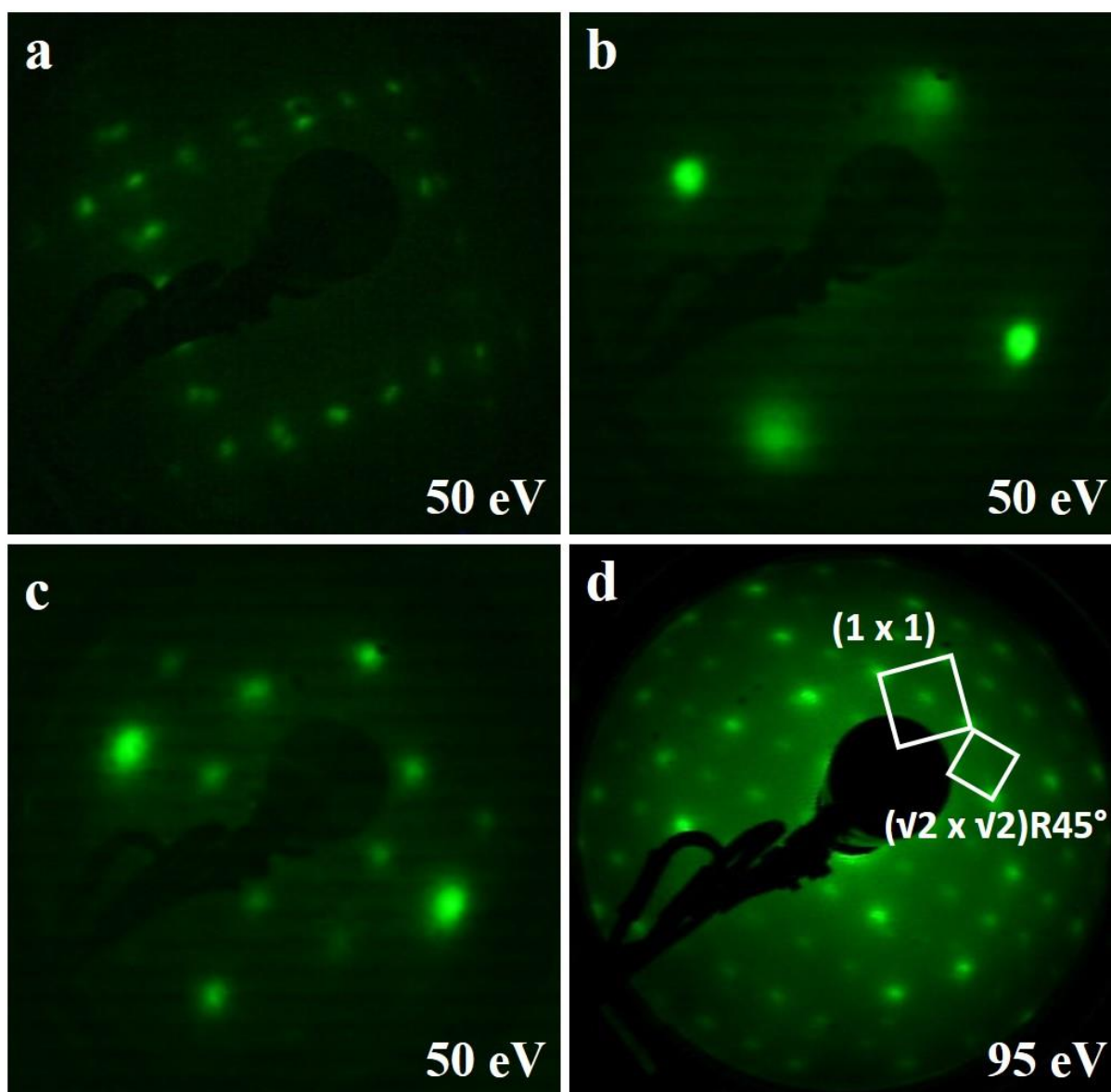


Figure 8.2. LEED patterns observed at the energies indicated for (a) the clean Pt(100) hex-reconstructed surface, (b) after deposition of a 4 nm thick Fe buffer layer, lifting the hex reconstruction and showing (1 x 1) pattern with the underlying Pt, (c) after reactive deposition of Fe in O₂ at 300 K as described in the text, and d) after the final annealing step described in the text. The annealing improves the sharpness of the observed spots, indicating a higher degree of surface ordering. The white squares in (d) show the (√2 x √2)R45° reconstruction.

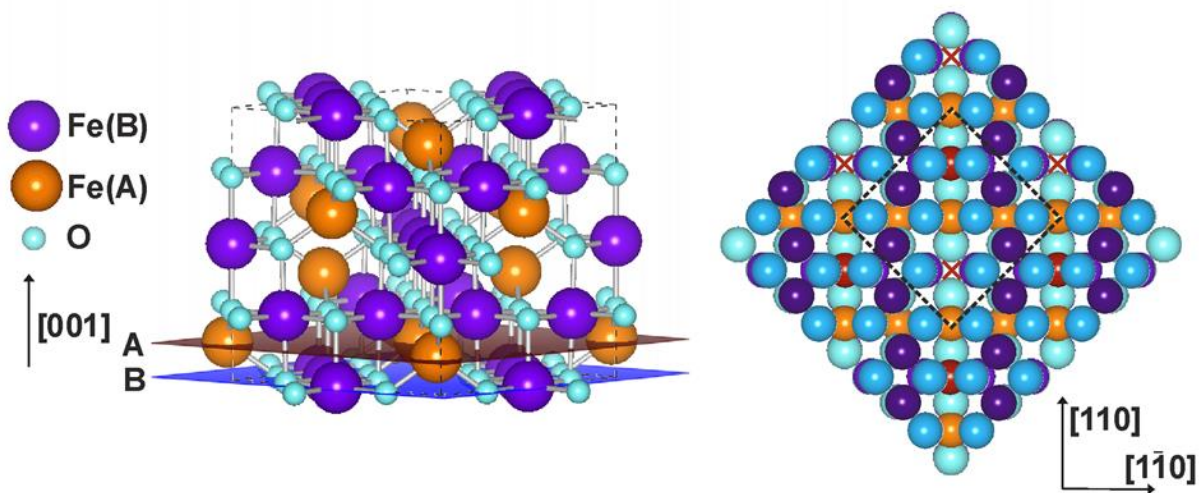


Figure 8.3. (a) Bulk structure of a unit cell of Fe_3O_4 indicating an A and B layer. Fe atoms are represented by the large orange (A-layer) and purple (B-layer) spheres and O atoms are represented by smaller blue spheres. (b) Top view of the $\text{Fe}_3\text{O}_4(100)$ surface with the suggested termination at a B-layer by Pentcheva et al.³⁶⁶ The red x's indicate the position of subsurface cation vacancies suggested by Bliem et al.³⁶⁰. Darker shading indicates atoms that are in the surface layer. This image was reproduced with permission from reference.³⁶²

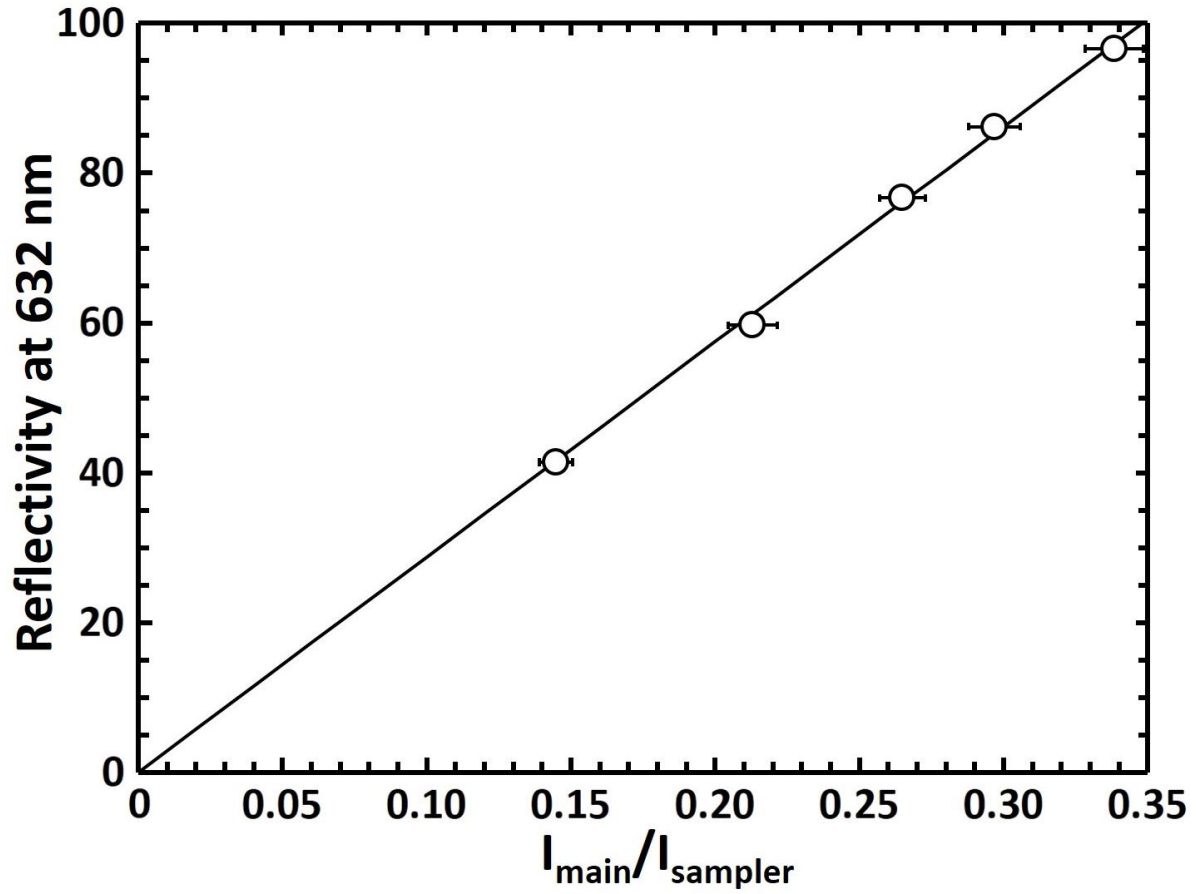


Figure 8.4. The calibration curve showing the dependence of the reflectivity of the mirrors with the photodiode intensity ratio $I_{\text{main}}/I_{\text{sampler}}$ as measured with a HeNe laser at 628 nm. The open circles indicate the average value of the intensity ratio for each mirror over 12 runs. The error bars represent the standard deviation of each point. The slope of the line is the average of the slope calculated in each of the 12 runs.

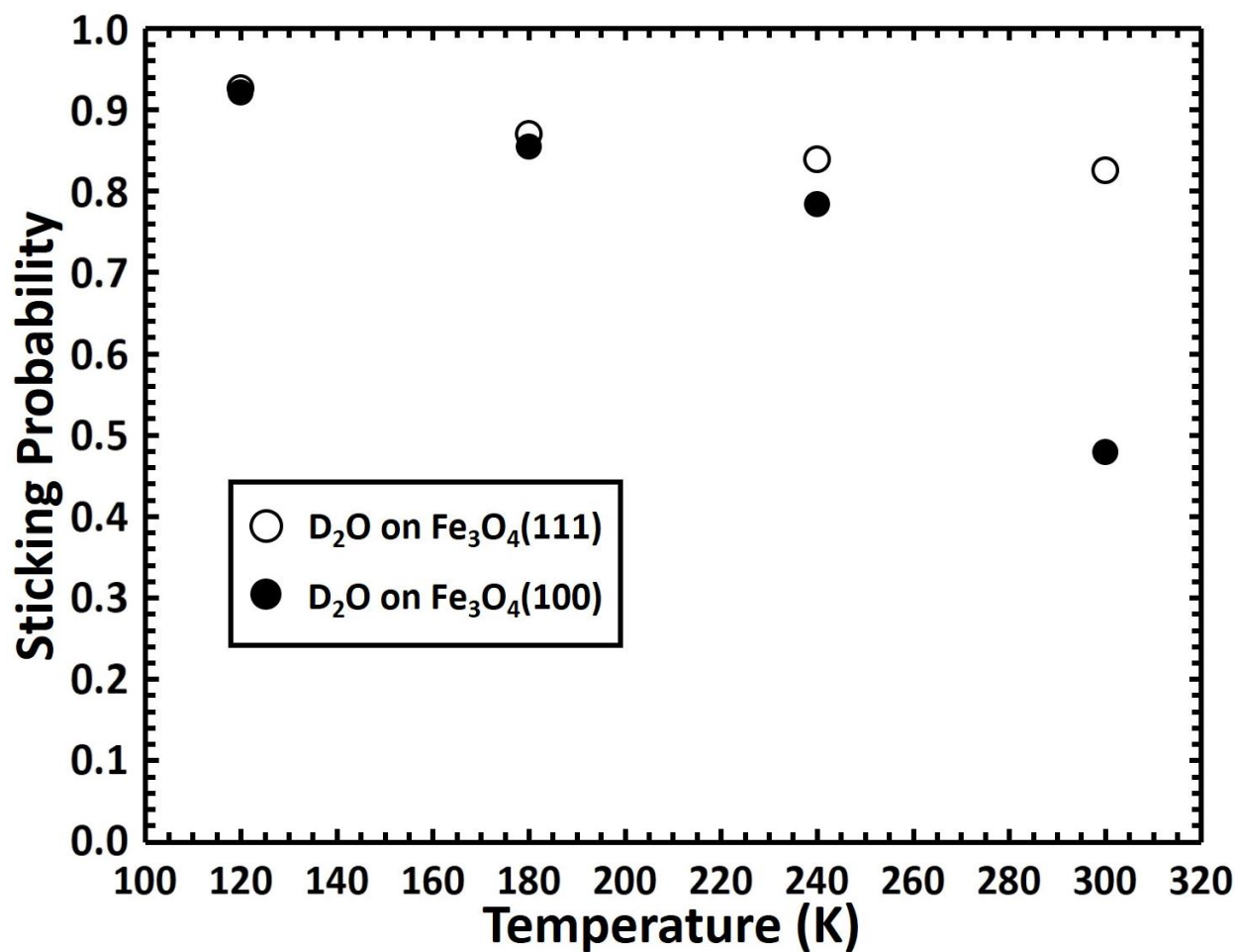


Figure 8.5. Short-term sticking probability of D₂O on Fe₃O₄(100) (closed circles) compared to Fe₃O₄(111) (open circles) as a function of sample temperature. This value represents the percentage of D₂O molecules that transiently adsorb to the surface but do not stick within the pulse window (266 ms), and this quantity remains constant at all coverages. The data points are averages over 10–15 experiments consisting of 20–50 D₂O pulses each.

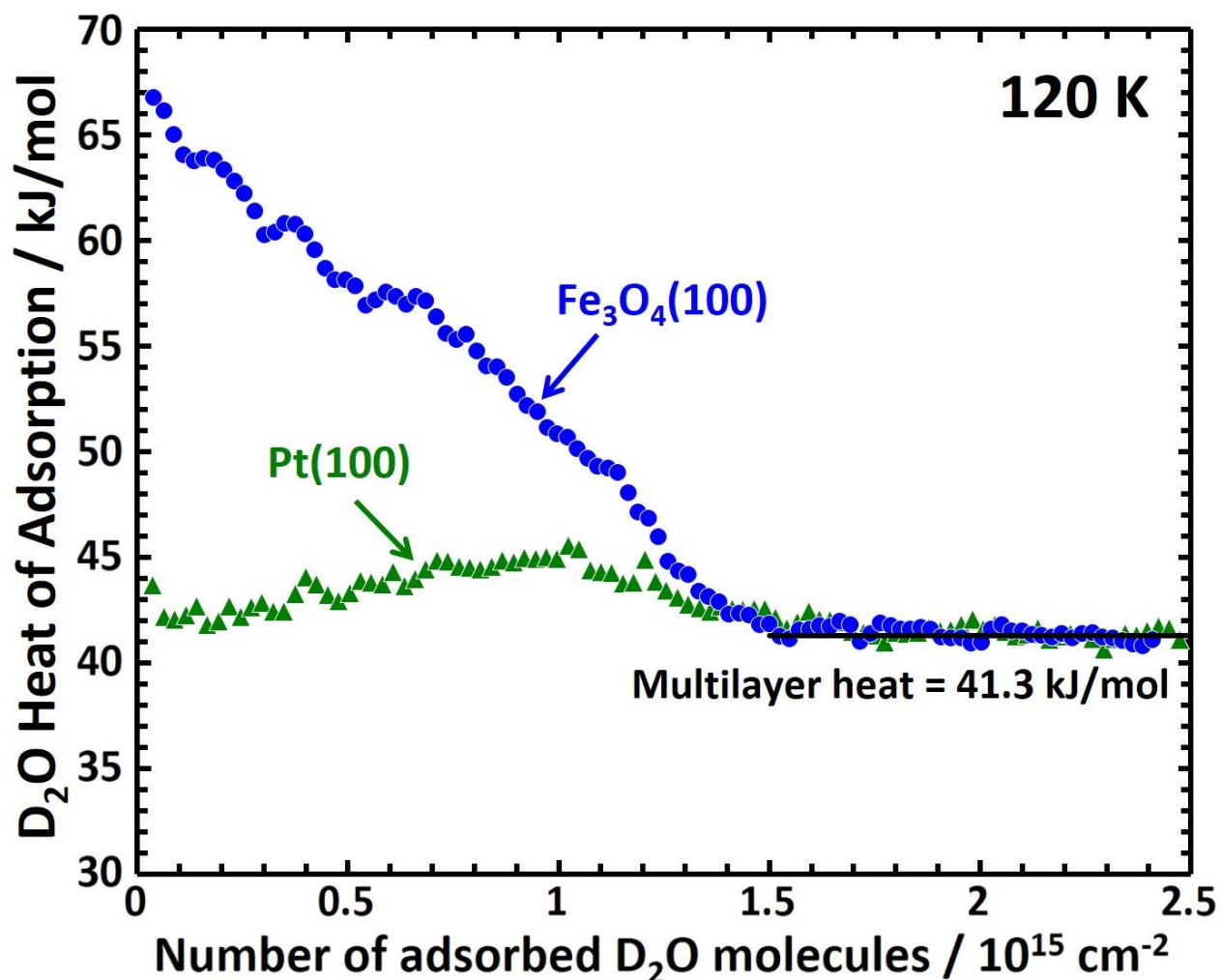


Figure 8.6. Heat of adsorption of D₂O as a function of the number of adsorbed molecules on bare Pt(100) (green triangles) and Fe₃O₄(100) / Pt(100) (blue circles) measured at 120 K. The data points are averages of 12–14 independent measurements. In both sets, the multilayer heat of 41.3 kJ/mol is reached by $\approx 1.4 \times 10^{15}$ D₂O molecules per cm², which is approximately the same value for the multilayer heat that was found on the (111) surface. Prior to this coverage, the heats on Pt(100) are only slightly higher as the first water layer forms, whereas the heats on the magnetite surface start high and decrease linearly, indicating a chemical interaction indicating likely water dissociation.

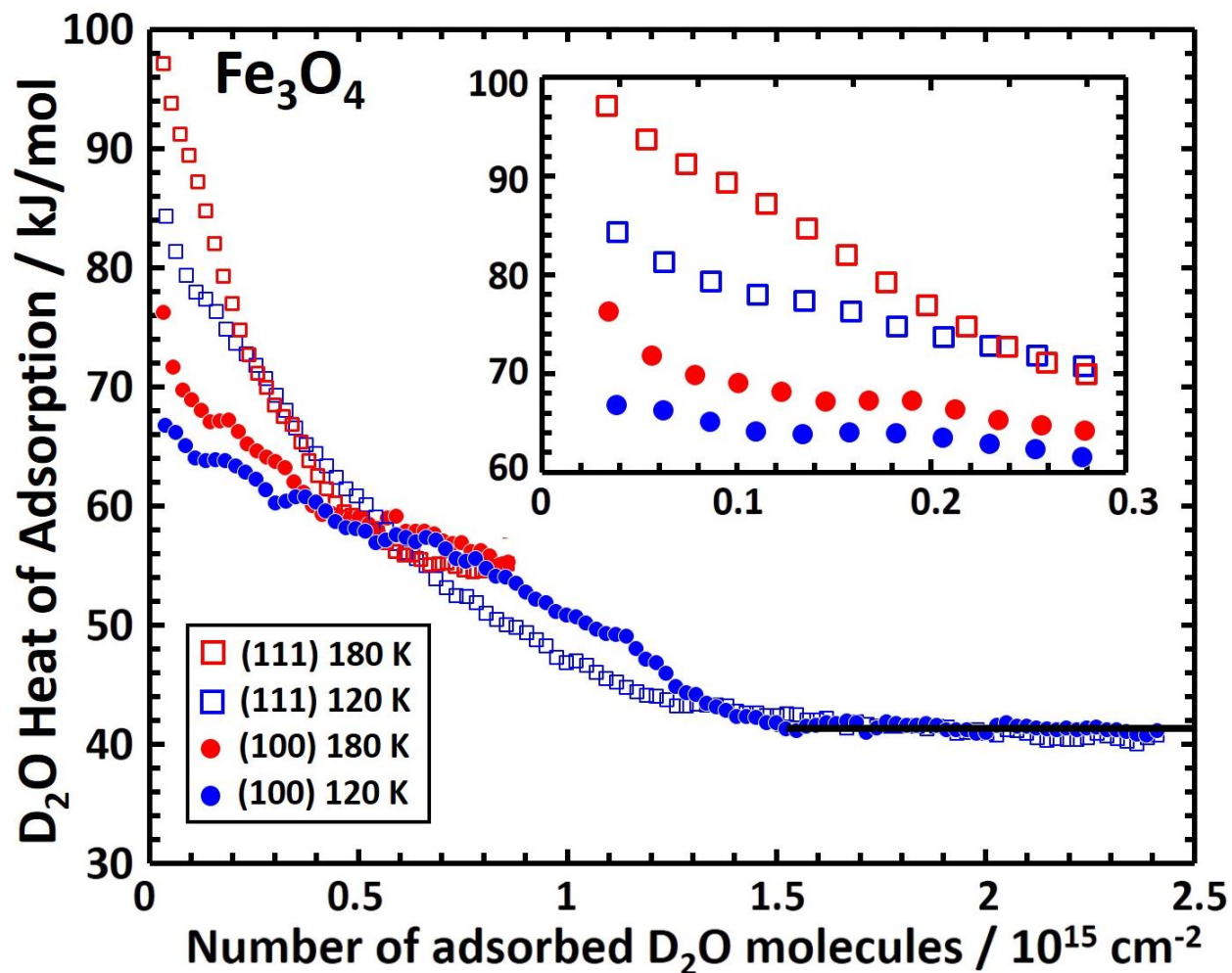


Figure 8.7. Heat of adsorption of D₂O as a function of the number of adsorbed molecules on Fe₃O₄(100) / Pt(100) (solid circles) compared to Fe₃O₄(111) / Pt(111) (open squares) measured at 120 K (blue) and 180 K (red). At 180 K, the heat data is not shown above $\approx 0.8 \times 10^{15} \text{ cm}^{-2}$ because the long-term sticking probability above this point is nearly zero, and this heat represents the equilibrium adsorption-desorption regime (therefore representing it as a function of increasing coverage is not physically reasonable). The heats of adsorption are higher at both temperatures on the (111) surface, indicating that this crystal face interacts more strongly with water than the (100) face. The data points are averages of 12–14 independent measurements.

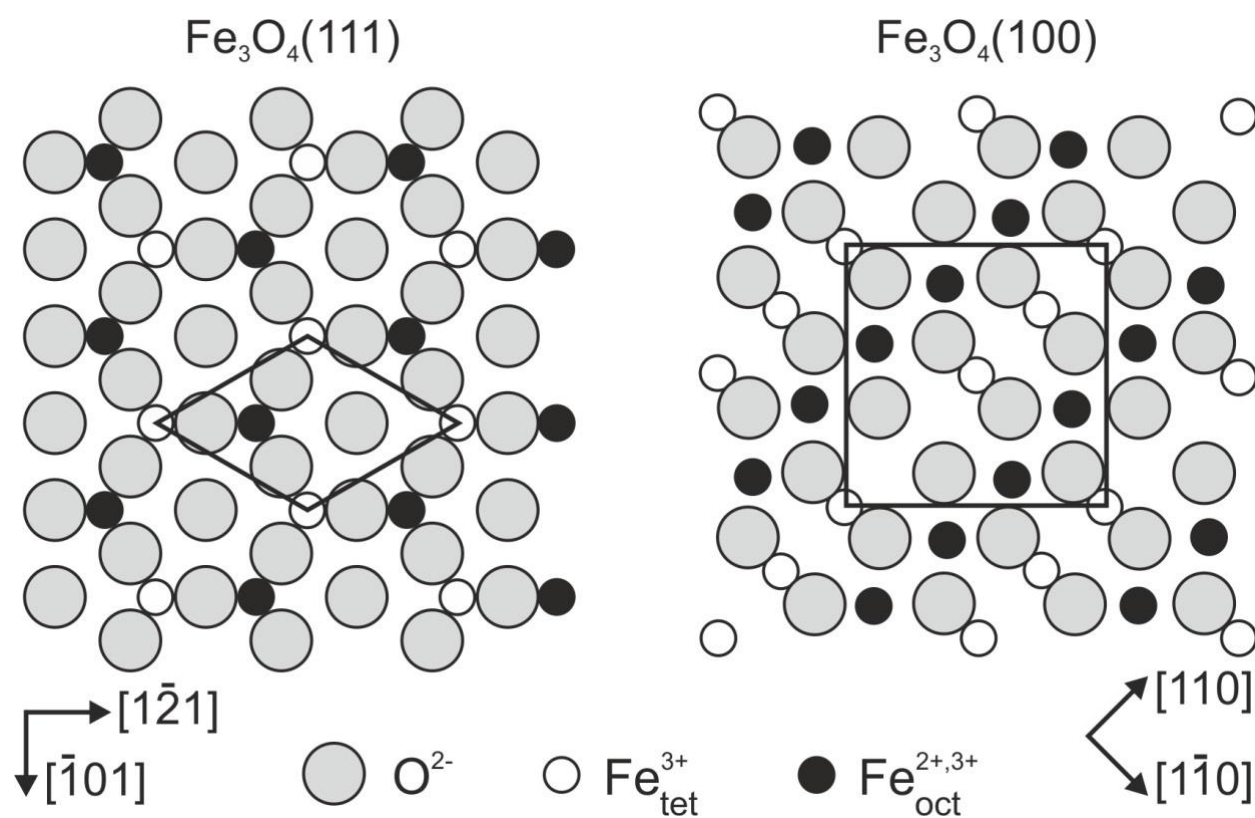


Figure 8.8. Top views of the $\text{Fe}_{\text{oct}2}\text{-Fe}_3\text{O}_4(111)$ and SCV- $\text{Fe}_3\text{O}_4(100)$ structural models. The black lines depicted are (1×1) hexagonal $\text{Fe}_3\text{O}_4(111)$ and $(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ $\text{Fe}_3\text{O}_4(100)$ surface unit cells.

Chapter 9. Conclusions and Future Outlook

The work presented in this dissertation represents a substantial step forward in the global effort to understand the catalytic properties of supported metal nanoparticle catalysts through fundamental, surface-specific investigations of well-defined model systems. Not only is SCAC a highly specialized and rare technique that is capable of benchmarking DFT calculations on systems that could not previously be studied experimentally, it also has proven capable of providing valuable insight into the growth morphology of metal films and nanoparticles, and to the critical role that defects and supports play in the properties of such materials. This work presents the first calorimetric investigation of the adsorption of gold atoms, nanoparticles, and films on three different substrates, and compares these results with other metals in the same column of the periodic table to help discover the nature of gold's unique properties.

Chapter 2 presented a summary of the key improvements to the newest UHV calorimeter that allowed this research group to study gold adsorption. These improvements included a reduction in background radiation enabled by an electron-beam heated metal vapor source and new geometry, as well as a technique to measure the change in metal atom flux continuously during an experiment.

Chapter 3 described the adsorption and adhesion of hemispherical Au nanoparticles on reduced ceria surfaces at 300 and 100 K. LEIS revealed that the Au particle density was nearly two times larger on the more reduced surface than on the more oxidized surface at 300 K, but nearly the same at 100 K. Surprisingly, when Au nanoparticles reached 2.5 nm in diameter on CeO_{1.80}(111) at 300 K, they thickened to an aspect ratio roughly twice as large as hemispherical caps, however this was *not* observed at 100 K, which indicated a thermally-limited step-up diffusion process. Au atoms adsorbed 37 kJ/mol more strongly to the more oxygen-deficient

CeO_{1.80}(111) surface than to CeO_{1.95}(111), which was also observed for Ag, indicating stronger binding of Au to oxygen vacancies than to the stoichiometric surface. The heat of Au atom adsorption at particle sizes under 1.5 nm is lower at 100 K than at 300 K due to stronger binding of Au to steps (which are less accessible at 100 K due to slower Au diffusion). The adhesion energy of 3.6 nm Au particles on CeO_{1.95}(111) was 2.53 J/m², and increased to 2.98 J/m² on CeO_{1.80}(111), albeit for smaller (2.6 nm diameter) particles.

Chapter 4 investigated the heat of Au adsorption onto MgO(100), which in many ways is considered a simpler surface than CeO_{2-x}(111). MgO(100) is non-reducible, highly stable, and very similar in structure to bulk MgO. However, investigation by LEIS combined with SCAC revealed a much more complex Au adsorption behavior that required additional support from the literature. The STM results of Benedetti et al.¹⁵² provided an interpretation of the LEIS data that revealed that Au grew as 2D bilayer thick islands below 0.4 ML. This was the first opportunity to measure the heat of adsorption of a metal atom onto a supported 2D metal particle as a function of its diameter. Above ≈ 0.4 ML, the diameter of these islands stopped changing significantly at an average value of ≈ 7 nm, where they thickened with coverage. At 300 K, the Au particle density was 3.0×10^{11} particles/cm² while it was 5.2×10^{11} at 100 K. At 300 K, the Au heat of adsorption for particles containing 31 atoms (285 kJ/mol,) was 68 kJ/mol higher than this value at 100 K, indicating that the measurements at 100 K are from Au particles at terraces, while at 300 K they are from Au particles nucleated at defects. The adhesion energy of 7 nm Au particles on MgO(100) at 300 K was 1.81 J/m², while at 100 K it was 0.31 J/m². The value at 100 K agrees significantly better with adhesion energy measurements found on this system using particle-shape techniques, which supports the conclusion that the adhesion energy at 100 K is for Au particles nucleated on MgO(100) terraces, whereas the much larger value at 300 K is due to particles at step edges and

kinks, or other defects. This project emphasizes the important role of morphological defects in adsorption behavior.

Chapter 5 presented a similar system to Chapter 3, where Cu adsorption was studied on $\text{CeO}_{2-x}(111)$. LEIS and XPS revealed that Cu grew as 3D particles with a fixed particle density of 7.8×10^{12} particles/cm² at all extents of reduction ($x = 0.05$ up to 0.2) at 300 K. The result that the particle density was not affected by the concentration of oxygen vacancies was opposite of what was observed for Au in Chapter 3, but similar to what was found for Ag, despite the fact that both Ag and Au adsorbed more strongly to reduced ceria.^{39,70,203} Cu atoms adsorbed initially more weakly to the more oxygen-deficient $\text{CeO}_{1.90}(111)$ and $\text{CeO}_{1.80}(111)$ surfaces (272 and 257 kJ/mol, respectively) than to the less oxygen-deficient $\text{CeO}_{1.95}(111)$ (300 kJ/mol). This was the first late transition metal studied by SCAC on any oxide to show this stronger bonding to stoichiometric sites compared to sites with oxygen vacancies. Above Cu particle diameters of 0.8 nm, incoming Cu atoms adsorbed with the same average heat of adsorption on all three ceria oxidation states, and increased with particle size to the bulk Cu(solid) heat of sublimation, which they reached at 2.2 nm. The adhesion energy of 2.2 nm Cu nanoparticles onto $\text{CeO}_{1.95}(111)$ at 300 K was 3.52 J/m² and decreased to 3.45 and 3.43 J/m² for $\text{CeO}_{1.90}(111)$ and $\text{CeO}_{1.80}(111)$, respectively.

Also in Chapter 5, the heat of adsorption of individual Cu atoms onto the terrace sites of $\text{CeO}_{1.95}(111)$ at 100 K was measured to be 224 kJ/mol. The particle density above 0.05 ML was 7-fold larger at 100 K (5.3×10^{13} particles/cm²) than at 300 K. The heat of Cu adsorption when making Cu nanoparticles with an average diameter of 0.45 to 0.8 nm is lower at 100 K than at 300 K by 50 to 30 kJ/mol on the same $\text{CeO}_{1.95}(111)$ surface, which was attributed to cluster nucleation on terrace sites at 100 K instead of the more stable step edge sites at 300 K. The measured chemical potential of Cu atoms versus Cu nanoparticle size at both terraces and step edges with $\approx 50\%$

oxygen vacancies was described. Since Cu is much less stable near oxygen vacancies on this surface, it avoided bonding near oxygen vacancies upon adsorption. Thus, the results for the smallest Cu clusters are not strongly influenced by the $\approx 2.5\%$ oxygen vacancies present on this $\text{CeO}_{1.95}$ surface, and the monomer and dimer energies are considered to be representative of stoichiometric $\text{CeO}_2(111)$ sites. Comparison to DFT+U calculations shows that calculated monomer adsorption energies differ from the experimental values by -44 to +69 kJ/mol.

Chapter 6 provided a comprehensive review of Cu, Ag, and Au adsorption and adhesion onto both $\text{MgO}(100)$ and $\text{CeO}_{2-x}(111)$ using the calorimetry results of the last 15 years combined with an analysis of the literature. This chapter detailed differences in growth morphology, relative affinity towards defects (including both morphological defects and oxygen vacancies), and the adhesion of these metals to these oxide surfaces. In general, $\text{CeO}_{2-x}(111)$ binds all of these metals more strongly than $\text{MgO}(100)$, and whereas Ag and Au bind more strongly to oxygen vacancies, Cu does not. This chapter proposed that the unique growth morphology of Au onto $\text{CeO}_{1.80}(111)$ and $\text{MgO}(100)$ reflects a strong interaction between the strongly electronegative Au and these electron-rich defects. Finally, a systematic trend was proposed between the adhesion energy of nanoparticles at the large-size limit onto oxide surfaces in UHV and the sum of the magnitudes of the metal's heat of sublimation plus the standard heat of formation of the most stable bulk oxide of that metal (per mole of metal atoms). This trend was initially proposed for $\text{MgO}(100)$ by the Campbell group in 2013, and was extended to include other oxide surfaces using both data presented in this dissertation and other UHV data from the literature. This trend may be applicable for metal adsorption to other oxides, and may offer a predictive trend in determining adhesion energy.

In Chapter 7, two model bimetallic systems were compared using SCAC, comprising of Cu layers on Pt(111) and Au layers on Pt(111). Single-crystal metal surfaces are far simpler and better understood than oxide surfaces. However systems in which one metal can alloy with another could not be studied by desorption techniques. Therefore, comparing these two systems revealed that some of the more fundamental differences between Cu and Au adsorption are based on their relative atomic size. Cu adsorbed onto Pt(111) with an initial heat of adsorption of 358 kJ/mol, and then decreased linearly in the first layer. This linear decrease was due to fewer Pt-Cu formed as the total Cu coverage increased, and the energy penalty from lattice strain in the topmost Pt and Cu layers. Recovery from this lattice strain caused the Cu heat of adsorption between 1 and 3 ML to be lower than Cu(metal) heat of sublimation. After 3 ML, the Cu heat of adsorption reached Cu(metal) heat of sublimation. Comparatively, Au (which is much larger, and closer in size to Pt) adsorbed onto Pt(111) with an initial heat of 382 kJ/mol, increased sharply to 393 kJ/mol by 0.03 ML, remained approximately constant until 0.7 ML, and then finally decreased linearly to the bulk heat of sublimation of Au(s) (368 kJ/mol¹⁸). This pattern of rise-level-fall was repeated from 1 - 2 ML and 2 - 3 ML, with decreasing values of constant energy in each step, and the sublimation of bulk Au(metal) was reached by 3 ML. The adhesion energy of the first ML of Cu to Pt(111) at 300 K was determined to be 3.84 J/m² and decreased to 3.76 J/m² by 4 ML. The adhesion energy of the first Au layer was found to be 3.57 J/m², and increased to 3.74 J/m² by 4 ML.

Finally, in Chapter 8, the adsorption of water onto well-defined thin Fe₃O₄(100) films was investigated using a calorimeter located at the Fritz Haber Institute in Berlin, Germany. This system was studied in order to investigate the role that oxide supports play directly in catalysis by examining the effect of surface structure on small molecule adsorption. Magnetite(100) films were grown on Pt(100), and their reflectivity was measured to be 65.2 ± 0.4%. The differential

adsorption energy of water was 67 ± 1 on $\text{Fe}_3\text{O}_4(100)$, and 42 ± 1 kJ/mol on $\text{Pt}(100)$ at 120 K. In contrast, water was previously found to have a stronger interaction with $\text{Fe}_3\text{O}_4(111)$ surface, with an initial adsorption energy of 87 ± 1 kJ/mol at 120 K. These data demonstrate that (100) surface has significantly lower reactivity towards water than the (111) surface. This difference was described in terms of the weaker Lewis acidity of its surface cation sites, which is caused by a smaller degree of coordinative unsaturation.

This dissertation builds on the work of innovative student researchers from the Campbell group over the last 15 years. The research presented here has added one of the most unique, most challenging, and most interesting metals to the library of thermodynamic and structural data that has been collected using SCAC, and has contributed significant fundamental insight to the greater surface science and catalysis community. These results have significantly improved our understanding of how the binding strength of metal atoms, nanoparticles and films on single crystal oxide and metal surfaces correlates to atomic and electronic structure, composition, and defect structure. These results will help the design and development of more efficient, longer lasting catalysts. Moving forward, the SCAC instrument will be used to study Pt adsorption onto these same oxide surfaces. Pt / ceria is the cornerstone material used in automotive catalytic converters, and Pt is one of the most active transition metals used in catalysis for the widest range of applications. Following this, the Campbell group hopes to use this instrument to study the adsorption of metals onto mixed metal oxides and carbon layers, to further bridge the gap towards more realistic materials used in catalysis applications. As we continue to probe more complex systems, we will expand the library of thermodynamic data available for DFT benchmarking, and we will use the fundamental insights gained in this dissertation to aid in the rational design of improved catalytic materials for our world's urgent and immediate energy applications.

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VITA

Stephanie Hemmingson originates from Portland, Oregon. She received a bachelor's degree in physics and chemistry from Kenyon College in 2008. Afterwards, she coordinated a multi-institutional MR Imaging research project under the guidance of Dr. Wei Huang and Dr. Alina Tudorica at the Advanced Imaging Research Center of the Oregon Health and Sciences University in Portland. During this time, she tutored school students in math and science at the Huntington Learning Center, and coached softball for Beaverton High School.

Stephanie conducted her PhD research under the supervision of Professor Charles Campbell. While at the University of Washington, Stephanie served one year as the president of the Chemistry Graduate Student Club, helping to institute the Chemistry Department's Individual Development Plan. She also joined the planning team for the 2015 Puget Sound Women Chemists retreat, and led the organization of the 2016 [expanded] Pacific Northwest Women in Science Retreat, a student-organized professional development symposium founded by Dr. Robbyn Anand with the support of the Northwest Region of the American Chemical Society.

During her graduate career, Stephanie mentored two undergraduate students, and was a teaching assistant for introductory chemistry (120, 121, 221), Physical Chemistry (455) and Statistical Mechanics (552). In the summer of 2014, Stephanie conducted research at Fritz Haber Institute in Berlin, Germany, where she worked under the supervision of Dr. Svetlana Schauermaun and Dr. Hans-Joachim Freund using a single crystal adsorption calorimeter that was built in collaboration with former students from the Campbell group.

Outside of the lab, Stephanie actively works to build opportunities for mentorship and support targeting women in science at the graduate, and professional level. She is particularly interested in how to develop scientists into innovators, and how to build collaborations between

academia, industry, and problem solvers across multiple arenas. To this end, Stephanie served for one year as the Vice President of Relations for the UW Science and Engineering Business Association, where she helped build connections to local tech communities in the Seattle area, and helped organize the UW Science and Technology Showcase in collaboration with the Burke Center for Entrepreneurship. Stephanie has also spent five years running the UW Graduate Chemistry Intramural softball team (the Ligand Fielders), which won its first ever championship in the summer of 2015. This is her proudest achievement to date.