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Gold-Surface-Mediated Hydrogenation Chemistry

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Dedication

To my parents and Beibei

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Gold-Surface-Mediated Hydrogenation Chemistry

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High surface area catalysts have been studied and applied in a wide range of chemical reactions and processes. The related microscopic details of surface chemistry are important and can be effectively explored employing surface science techniques. My dissertation focuses on investigations of catalytic properties of gold, primarily using vacuum molecular beam techniques, temperature programmed desorption (TPD) measurements, reflection-absorption infrared spectroscopy (RAIRS), and density functional theory (DFT) calculations.

I conducted fundamental studies of hydrogenation reactions on a H atoms precovered Au(111) single crystal surface with co-adsorption of various chemical compounds, including acetaldehyde (CH₃CHO), acetone (CH₃COCH₃), propionaldehyde (CH₃CH₂CHO), water (H₂O), and nitrogen dioxide (NO₂). These studies allow better understanding of hydrogenative conversions facilitated by gold catalysts, which show great promise in hydrogenation applications but for which relevant fundamental studies are lacking. The experimental results unravel the unique and remarkable catalytic activity of gold in hydrogenation reactions: *i*) H atoms weakly absorb on the Au(111) surface and have a low desorption activation energy of ~ 28 kJ/mol; *ii*) acetaldehyde can be hydrogenated to ethanol at a low temperature of < 200 K; *iiii*) propionaldehyde can be hydrogenated to 1-proponal (CH₃CH₂CH₂OH) on H pre-covered Au(111) whereas 2propanol (CH₃CH(OH)CH₃) cannot be formed in the reaction of acetone with hydrogen atoms; *iv*) a coupling reaction of aldehyde-aldehyde or aldehyde-alcohol is observed on the H pre-covered Au(111) surface at temperatures lower than 200 K and this reaction can produce various ethers (symmetrical or unsymmetrical) from aldehydes and alcohols with the corresponding chain length; v) co-adsorbed H atoms have a strong interaction with water on the gold model surface and induce the dissociation of the O-H bond in water, which cannot be dissociated on the clean surface; vi) we observed a facile reaction of NO₂ reduction on H covered Au(111) and NO is produced at 77 K, yielding high NO₂ (100 %) conversion and selectivity towards NO (100 %) upon heating the surface to ~ 120 K.

These studies indicate the exceptional catalytic activity of gold and enhance the understanding of surface chemistry of classical supported Au-based catalysts at the molecular scale.

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Chapter 1: Introduction

Heterogeneous catalysis is one of the most important processes in the modern chemical industry and its application is extremely widespread. In principle, a catalyst can reduce the energy barrier to overcome for driving a chemical reaction, consequently accelerating the reaction rate and increasing the yield of targeted products.¹ In order to design and prepare catalysts with high reactivity and selectivity, fundamental studies, including surface area, active sites, exposed facets, and particle size distribution, have become the focus of attention from researchers. By definition, heterogeneous catalysis refers to reactions happening on the surfaces of catalysts. However, complicating factors such as molecule adsorption, diffusion, reaction, and desorption on the surface combine to yield a complicated catalytic process, which makes it difficult to reveal the reaction mechanism associated with various catalyst properties.

Surface science, employing model catalytic systems and ultrahigh vacuum (UHV, $\sim 10^{-10}$ torr) conditions, allows us to study realistic high surface area catalysts in a better characterized system.² Well-defined single crystals as well as deposited nano-scaled thin films or particles could simplify the investigations of reactions by manifesting some specific properties of catalysts. In order to conduct experiments properly, UHV is necessary to keep the surface clean by reducing the possibility that molecular contaminants (from the residual gas atmosphere) adsorb on the sample surfaces. Additionally, most techniques for surface science, such as quadrupole mass spectrometry (QMS), scanning tunneling microscope (STM), auger electron spectroscopy (XPS), etc., require the use of free electrons or ions as detection probes. Therefore, UHV conditions are also useful for increasing their mean free path to diminish the mutual interferences.³

Thus, surface science offers an opportunity for *in-situ* studies of reactions via the collection of direct detailed information regarding the catalytic mechanism.



Figure 1.1: The correlation between the studies on model and classical catalytic systems.⁴⁻⁶

Figure 1.1 demonstrates the relationship between model catalysts and realistic classical catalysts. The *y*-axis indicates catalyst complexity, from the simplest model catalytic system – single crystal sample with an uniform surface structure,⁴ to multi-component model catalysts – nanoparticles supported on a well-surface-structured sample (metal or metal oxide),⁵ to classical high surface area supported catalysts used in practical applications.⁶ Moreover, the *x*-axis represents reaction conditions from low to high temperatures and pressures. For comprehensively understanding fundamentals of a classical catalyst in order to further improve catalyst design and enhance activity, many

parameters need to be considered, such as surface area, particle sizes and shapes, and the role of metals, supports and interfaces. It is very difficult to isolate one of those parameters and specifically study it without considering other effects. Thus, with well-ordered surface structure, a model catalyst could be used to approach the related fundamental information of one aspect of the catalyst. Further, more detailed information can be collected from a variety of model catalysts and combined to obtain a more holistic understanding of the corresponding classical catalytic system. In addition, a model catalytic study is able to discover new chemical reactions since vacuum conditions establishes a clean background and increases the sensitivity of detection of species. Therefore, a reaction with low conversion and reactivity is still able to be detected and this reaction can be further studied in more detail on the relevant high-surface area classical catalysts. Overall, classical catalytic systems raise fundamental questions, and model systems can provide the answers and feedback to enhance a better understanding.

In this dissertation, I demonstrate a series of fundamental studies of hydrogenation reactions on a model gold surface, Au(111). This work aims to understand the role of gold in hydrogenation transformations, which has been widely investigated on classical gold-based catalysts but the fundamental understanding is lacking.

ADVANCES IN HYDROGENATION REACTIONS ON CLASSICAL GOLD CATALYSTS

Historically, gold has been considered catalytically inert. However, in recent decades, highly dispersed nano-scale gold particles supported on metal oxides have been synthesized and found to exhibit unexpectedly high activity for some chemical reactions. In pioneering work, Haruta discovered that gold nanoparticle catalysts have extraordinary activity for CO oxidation.⁷ This work prompted numerous follow up studies, and to date, gold-based heterogeneous catalysts have shown a high activity for many oxidation

reactions.^{8,9} Related fundamental studies have also been extensively conducted both experimentally¹⁰⁻¹² and theoretically.^{13,14}

Additionally, gold-based catalysts have also been studied in hydrogenation reactions. Bond *et al.* employed supported gold catalysts for selective hydrogenation of 1,3-butadiene¹⁵ and later Hutchings *et al.* studied hydrochlorination of acetylene¹⁶ over gold. To date, many studies have been conducted for several other hydrogenation reactions on gold-based catalysts as well.^{17,18} Gold can be used as a catalyst for hydrogenation of various hydrocarbons with one or more unsaturated bonds (i.e. C=C, C=C, C=O, and C=O), such as CO,¹⁹ CO₂,²⁰ acyclic alkenes,²¹ cyclic alkenes,²² alkynes,²³ derivatives of benzene,²⁴ and unsaturated aldehydes.²⁵

The physical properties of gold-based catalysts have been studied with respect to the activity of hydrogenation reactions. Gates and co-workers claimed that, in a general point of view, hydrogenation of hydrocarbons is structure insensitive over most metal catalysts,²⁶ in agreement with results obtained by Haruta *et al.* on Au catalysts in the hydrogenation of 1,3-butadiene.^{27,28} However, a different phenomenon has been observed by Hensen and co-workers in which very small gold clusters of a few Au atoms supported by ceria show a remarkable activity, at least one order of magnitude greater than nanometer-sized gold particles in the hydrogenation of 1,3-butadiene.²⁹ The dependence of the activity on gold particle size has also been addressed for hydrogenation of other hydrocarbons. Nikolaev *et al.* prepared Au/Al₂O₃ with a variety of gold particle sizes, ranging from 2.5 to 30 nm, for the selective hydrogenation of phenylacetylene into styrene. They found that with decreasing particle size from 30 to 2.5 nm, the turnover frequency (TOF) increases by a factor of 5 and the selectivity of styrene increases by a factor of 10.^{30,31} In crotonaldehyde hydrogenation to crotyl alcohol on Au/TiO₂, Touroude *et al.* noted that the TOF depends on the gold particle size and

drastically increases when the particle diameter reduces to 2 nm.³² It is likely that the smaller gold particle/cluster yields the higher activity of hydrogenation. Claus argued that this structural sensitivity is due to the quantum-size effect of sufficiently small gold particles.³³ In an extreme case based on theoretical calculations, Liu *et al.* elucidated that a single gold atom is active for the hydrogenation of 1,3-butadiene.³⁴ Effects of gold valence state have also been investigated for hydrogenation reactions. Zhang and co-workers reported that isolated Au³⁺ ions at the surface of ZrO₂ is more active for the hydrogenation of 1,3-butadiene of 1,3-butadiene for the hydrogenation of 1,3-butadiene compared to metallic gold.^{35,36}

In the case of hydrocarbons containing more than one unsaturated bond, gold shows extraordinary selectivity for partial reduction. By exploring catalytic properties of gold for the hydrogenation of α,β -unsaturated nitrocompounds, Corma revealed the exceptional reactivity of Au/TiO₂ to produce oximes over Pd and Pt catalysts.³⁷ Bonds et al. observed 60 % of selectivity for 1-butene over Au/boehmite in the hydrogenation of 1,3-butadiene¹⁵ (20 % for *cis*-2-butene and 20 % for *trans*-2-butene). The same reaction has been conducted on Au/SiO₂ both experimentally and theoretically by Li and coworkers, also showing ~ 60 % of selectivity for 1-butene but production of cis-2-butene is more favorable than the trans isomer (cis/trans ratio changed from 5.3 to 1.5 with increasing gold particle size from 2.7 to 9.1 nm).³⁸ In the hydrogenation of unsaturated aldehydes such as acrolein, the C=C group thermodynamically favors hydrogenation compared to the C=O bond.¹⁷ However, according to the commercial demand, allylic alcohols are desirable to be manufactured preferentially via enhancing the intromolecular selectivity of the C=O rather than C=C bond. Claus and co-workers studied gold-based catalysts for this reaction, demonstrating that gold is more active toward C=O hydrogenation compared to platinum catalysts (The selectivity on Pt/ZrO₂ is about one tenth of that on Au/ZrO₂).¹⁷ The structural effects of gold particles were also investigated.³⁹ They deposited gold particles with the same diameters on TiO₂, SiO₂, ZrO₂ and ZnO, observing that Au particles are nearly spherical on TiO₂ and SiO₂ whereas they showed extended facets on ZrO₂ and ZnO.⁴⁰ The higher degree of particle rounding results in the higher selectivity for allylic alcohols, indicative of the importance of low-coordinated surface sites.⁴¹ Thus, Au/ZnO has been modified by employing indium to cover gold particle faces (to deactivate the C=C hydrogenation) and leave edges free, yielding a promoted selectivity of 63 % for the desired allyl alcohol.⁴² This finding provided evidence that the edges of single crystalline gold particles are active sites for the selective C=O hydrogenation. However, Kang and co-workers argued based on DFT calculations that the high selectivity of allyl alcohols on indium decorated Au catalysts is due to the strong interaction of indium with oxygen in acrolein while the C=C hydrogenation is favorable at edges and corners.⁴³

Among the Group VIII metals, palladium and platinum are more reactive for many reactions compared to gold, and accordingly have been used to prepare bimetallic catalysts with gold in order to enhance reactivity of gold catalysts. Pd-Au alloy catalysts have been studied in a wide range of applications.⁴⁴ Addition of palladium can improve the activity of gold catalysts significantly in hydrogenation reactions of hydrocarbons and their derivatives such as acetylene,⁴⁵ citral,⁴⁶ and p-chloronitrobenzene.⁴⁷ Neurock *et al.* conducted theoretical calculations regarding the hydrogenation of ethylene on Pd/Au(111) and found that increasing Au composition can weaken the metal-hydrogen and metal-carbon bonds to enhance the intrinsic activity for hydrogenation and suppress H₂ adsorption and activation. Balancing these two effects can yield an optimum reactivity of hydrogenation.^{48,49} On the other hand, by alloying platinum with gold over TiO₂ to promote H₂ dissociation, Corma and co-workders developed an excellent catalyst for the hydrogenation of nitroaromatic compounds.⁵⁰

For hydrogenation over gold-based catalysts, H_2 dissociation has been generally considered as a rate-limiting step.^{9,51} Monitoring the production of HD from hydrogen and deuterium exchange, H_2 interaction with gold catalysts was investigated.⁵² Over Au/Al₂O₃, Bus and co-workers⁵³ found that hydrogen dissociation and activation is activated, preferably mediated by edges and corners of gold particles, in agreement with Nieuwenhuys results.⁵⁴ Additionally, Corma *et al.* claimed, based on DFT calculations over Au/TiO₂, that only neutral or nearly neutral gold atoms on low coordinated positions are active for hydrogen dissociation.⁵⁵ However, Haruta and co-workers carried out the H₂-D₂ exchange reaction on various surfaces [Au(111), Au(311), TiO₂(110), and Au/TiO₂(110)] and suggested that the active sites for H₂ dissociation are actually at the interface between the gold particles and TiO₂ support. They also noted the correlation between the activity and gold particles size: the smaller gold particles contribute to the higher activity for H₂ dissociation.⁵⁶

In summary, gold-based catalysts show great promise in applications for selective hydrogenation processes. As we discussed above, three of the most prominent examples are: 1) selective hydrogenation of acetylene to ethylene with a selectivity higher than 90 %;⁵⁷ 2) Chemoselective hydrogenation of unsaturated aldehydes (such as acrolein) to yield unsaturated alcohols with 10 times higher activity than traditional platinum-based catalysts;⁴² and 3) For nitro-unsaturated molecules, NO₂ groups have a high chemoselectivity (> 95 %) compared to other unsaturated functional groups present on the molecule, such as C=C, C=O, C=N, and benzene groups.^{4,58}

Gold-based catalysts show intriguing activity for hydrogenation reactions. We speculate that a single H atom is likely one of the more active species on gold surfaces since it is very weakly bound. This phenomenon is likely similar to the observations of O on gold: model studies indicate that oxygen atoms have a weaker interaction with Au surfaces compared to other metallic surfaces, leading to extraordinary activity for selective oxidation reactions.^{59,60} Thus, in order to verify this speculation and explore the related reaction mechanisms, fundamental studies of hydrogenation transformations with H on Au surfaces are needed.

ADVANCES IN HYDROGENATION ON MODEL SURFACES

In order to obtain a more fundamental understanding of hydrogenation reactions on gold-based catalysts, surface chemistry of the gold single crystal has been studied under ultrahigh vacuum (UHV) conditions. To date, little work has been reported on the gold single crystal regarding hydrogen adsorption and hydrogenation reactions. H₂ dissociation has a high barrier⁶¹ on gold surfaces and atomic hydrogen is necessary to populate the gold model surface for the study of hydrogenation reactions. Sault, Madix, and Campbell⁶² adsorbed hydrogen atoms, which were generated by the mass spectrometer filament, on clean Au(110) and observed a hydrogen desorption feature at 216 K by using temperature programmed desorption (TPD) techniques. Since the (111) facet is most stable and readily formed in classical heat-treated gold catalysts, Au(111) has become a desired model surface to study hydrogenation reactions from a mechanistic point of view. Rettner et al. investigated the reaction of an H-atom beam with Cl precovered $Au(111)^{63,64}$ but he didn't address the desorption of hydrogen on the clean Au(111) surface. Therefore, it was still unknown until recently whether H atoms can adsorb on Au(111) and what chemistry on the Au(111) surface is related to hydrogenation reactions. Mavrikakis et al.⁶⁵ used DFT calculations to predict that the H binding energy is - 2.22 eV on Au(111), lower than that on Ag(111) and Cu(111). Furthermore, experimental results demonstrated the adsorption of H atoms on Cu(111)⁶⁶ and Ag(111),⁶⁷ respectively, suggesting the possibility of adsorbed H atoms on Au(111).

	Desorption peak		
Metal surfaces	Hydrogen source	temperatures	References
Au(111)	Atomic	111 K	68
Au(110)	Atomic	216 K	62
Ag(111)	Atomic	160 K	67
Ag(100)	Atomic	110 K, 120 K, 150 K	67
Cu(111) (D)*	Atomic	350 K	66
Al(100)	Atomic	310 - 340 K	69
Ni(111)	Molecular	310 K, 380 K	70
Ni(100)	Molecular	360 - 400 K	70
Ni(110)	Molecular	350 K	70
Pd(111)	Molecular	205 K, 280 - 310 K	71
Ir(111)	Molecular	270 - 380 K	72
Ir(110)	Molecular	200 - 300 K, 400 K	73
Pt(111)	Molecular	280 - 350 K	74
Ru(001)	Molecular	320 - 420 K	75
Mo(110)	Molecular	500 - 650 K	76
W(110)	Molecular	440 - 510 K	77
Fe(110) (D)*	Molecular	450 K	78

*Deuterium is employed in TPD measurements

Table 1.1: Desorption of molecular H_2 on transitional metal surfaces.

H₂ desorption temperatures can also vary widely between the different faces of the same metal. For example, H_2 desorption temperature from Au(111) (which will be discussed in detail in Chapter 2) is much lower than the desorption from Au(110) at 216 K, indicating a higher desorption activation energy on Au(110) of ~ 51 kJ/mol.⁶² This comparison clearly demonstrates that the surface structure can significantly affect H desorption from gold. The kind of metal and its various surface structures are closely associated with its catalytic properties and play a key role in determining the surface chemistry for chemical reactions. Therefore, it is educational to examine the peak desorption temperatures, as shown in Table 1.1, for H₂ desorption from a variety of metal surfaces. The desorption temperatures suggest the binding energy of H on these various metal surfaces increases roughly in the order of Au < Ag < Cu, Al, Ni, Pd, Pt, Ir, Ru < Mo, W, Fe. From DFT calculations,⁶⁵ H atoms have a small binding energy on Ag(111), Au(111), and Cu(111). This is consistent with the TPD measurements, in which H_2 immeasurably dissociatively adsorbs on those surfaces and atomic hydrogen has been employed, as shown in the "Hydrogen Source" column in Table 1.1. However, it should be noted that the H_2 desorption temperature on Cu(111) is much higher than that on Au and Ag.

There are multiple desorption features on some metallic surfaces, where the low temperature peaks are due to subsurface H desorption from H atoms that diffuse into the bulk. These sub-surface H features appear with increasing coverage of hydrogen on the surface and can even be larger than the saturated surface H desorption feature. Note that two peaks are observed for subsurface H desorption on Ag(100) at 110 and 120 K, possibly due to surface reconstruction during the adsorption of H. In addition, on some metal surfaces such as Pd, Ir, Pt, W, Ru, and Mo, molecular hydrogen can dissociatively adsorb on the surface and lead to second-order kinetics for the recombinative desorption

rate, which results in the peak temperature shifting from high temperatures to low temperatures with increasing coverages. Therefore, Table 1.1 provides a temperature range for H_2 desorption from those surfaces.

OVERVIEW OF DISSERTATION

In this work, we employed atomic hydrogen and co-adsorbed it with various chemical compounds on the Au(111) model surface in order to access mechanistic information for those reactions and better understand the hydrogenative activity of gold-based catalysts. This study is divided into five chapters, Chapters 2 - 6, which resulted in five peer-reviewed journal articles.^{68,79-82}

Chapter 2 describes the adsorption and desorption of hydrogen on Au(111) and hydrogenation of acetaldehyde to ethanol. To our best knowledge, this was the first reaction which has been reported on a model Au(111) surface regarding hydrogenation reactions, and this reaction can be considered as a probe reaction to show the hydrogenative surface chemistry of gold. Here, we show that chemisorbed hydrogen adatoms bind weakly to the gold surface, with a desorption peak at ~ 110 K, indicating an activation energy for recombinative desorption of ~ 28 kJ/mol. We further demonstrate that acetaldehyde (CH₃CHO) can be hydrogenated to ethanol (CH₃CH₂OH) on the H atom pre-covered Au(111) surface at low temperatures. Isotopic experiments employing D atoms indicate a lower hydrogenation reactivity, suggesting kinetic isotope effects.

Chapter 3 presents results comparing propionaldehyde and acetone hydrogenation on the Au(111) surface. A mechanistic understanding of hydrogenation of C=O bonds can provide fundamental information about chemoselectivity during hydrogenation of unsaturated carbonyls. Here we demonstrate the chemoselective reactivity of acetone and propionaldehyde on H-covered gold. The experimental results indicate that propionaldehyde can be hydrogenated to 1-propanol. In contrast, no hydrogenated product has been detected from the interaction between acetone and hydrogen. DFT (density functional theory) calculations predict dissimilar energetic barriers for the individual steps in the hydrogenation reaction and indicate the basis of the chemoselective activity. The polymerization of CH₃CH₂CHO is also found to play a role in the hydrogenation of propionaldehyde by increasing the concentration of CH₃CH₂CHO at elevated temperatures. In addition, the production of di-n-propyl ether from propionaldehyde is noted at temperatures above 200 K.

Since ether formation is observed from the reaction between propioanldehyde and hydrogen on Au(111), as discussed in Chapter 3, Chapter 4 describes an extensive study of ether synthesis with H and aldehydes on Au(111). We demonstrate the synthesis of ethers via heterogeneous-catalysis over H adatom-covered gold at temperatures lower than 250 K. Symmetrical ethers can be formed via a self-coupling reaction of corresponding aldehydes, for example, homo-coupling of acetaldehyde and propionaldehyde give diethyl ether and di-n-propyl ether, respectively. In addition, coupling reactions between alcohols and aldehydes are observed with production of the corresponding unsymmetrical ethers. A reaction mechanism is proposed, suggesting that an alcohol-like intermediate via partial hydrogenation of aldehydes on the surface plays a key role in these reactions.

Chapter 5 presents a fundamental understanding of the interactions between coadsorbed water and hydrogen on metallic surfaces, which is critical to many chemical processes including catalysis and electrochemistry. Here, we report on the strong and intricate interactions between co-adsorbed H/D and water on the close-packed (111) surface of gold. Deuterium isotopic labeling shows H-D exchange in H-D₂O and D-H₂O systems, indicating water dissociation and suggesting a non-random scrambling process
by revealing the origin of hydrogen evolution (from surface H atoms or from water molecules) during TPD. In this reaction, the protonation of the H-bonding ice network (i.e., the formation of $(H_2O)_nH^+$) is energetically favorable and is responsible for water dissociation. Density functional theory (DFT) modeling suggests that the thermodynamics and structure of the protonated clusters are predominant factors for yielding the traceable H₂ desorption features from the surface interaction with H atoms, providing insights into reaction mechanisms.

The most recent study is NO₂ reduction on H covered Au(111), which is described in Chapter 6. In this work, we have discovered that NO₂ is reduced to NO at 77 K by hydrogen pre-covered gold in vacuum. NO_x reduction is crucial to control and abatement of transportation emissions and air pollution. Here, we investigate NO₂ reduction on an atomic-hydrogen populated model gold catalyst for a more fundamental understanding of the surface chemistry of hydrogenation. Our experimental results reveal a high catalytic activity for gold: NO₂ is reduced to NO with 100 % conversion and 100 % selectivity at temperatures lower than 120 K. Density functional theory (DFT) calculations and reflection-absorption infrared spectroscopy measurements (RAIRS) indicate that HNO₂ and N₂O₃ are intermediates which are highly dependent on surface hydrogen concentrations; subsequent hydrogenation of HNO₂ and dissociation of N₂O₃ upon annealing induces the production of NO and H₂O.

Finally, Chapter 7 summarizes our work in hydrogenation on a gold model surface, where the conclusions are briefly addressed. Further, since atomic hydrogen is required for the study of hydrogenation on gold, the practical impact is discussed, especially whether generated H atoms from H_2 dissociation on other surface sites such as defects or interfaces can migrate/spill over onto the Au face sites for driving chemical reactions, as studied in this dissertation. In addition, recommendations for future work are

provided regarding the establishment of the gap between gold model and classical catalysts.

Additionally, there are two studies on an iridium (111) sample surface in the Appendices, demonstrating CO dissociation and the interaction of water with oxygen. These studies led to two journal papers.^{83,84} Appendix A describes our work on CO dissociation at low temperatures (less than 400 K) on Ir(111) under ultrahigh vacuum (UHV) conditions. Although CO does not dissociate on the clean Ir(111) surface, the addition of atomic oxygen induces CO dissociation. Similarly, CO dissociation has also been observed on water pre-covered Ir(111) or water and oxygen pre-covered Ir(111), which stems from effects of hydroxyl groups produced by the interaction of water and oxygen.

Appendix B presents results on adsorption and reaction of water on the clean and oxygen modified Ir(111) single crystal surface using temperature programmed desorption (TPD) and molecular beam reactive scattering (MBRS) techniques under ultra high vacuum (UHV) conditions. Water dissociates on the clean Ir(111) surface with a probability (estimated based on production of hydrogen) which decreases from ~ 0.016 to 0.004 \pm 0.0015 with increasing water coverages from 0.34 to 2.59 monolayer. Scattering experiments performed at various surface temperatures in the limit of zero coverage yield water dissociation probabilities in the range ~ 0.0005 – 0.012 (300 - 900 K) with an uncertainty expressed as \pm 20 % of the dissociation probability. The apparent activation energy for water dissociation on clean Ir(111) is estimated to be approximately 170 \pm 5 kJ/mol employing MBRS techniques, which probably cannot be applied to TPD measurements with higher water coverages. We speculate that water dissociation occurs on the defects of the Ir(111) surface. Using isotopically labeled reactants, a strong

interaction between adsorbed water and oxygen was found on Ir(111), indicated by a new water desorption feature at 235 K and scrambled oxygen and water desorption products.

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Chapter 2: Hydrogenation of Acetaldehyde to Ethanol

INTRODUCTION

The high catalytic activity of nano-scale gold has been discovered by discovered by Haruta,¹⁻³ Hutchings,⁴ and Bond.⁵ To date the studies on gold catalysts have been widely conducted for many oxidation reactions including CO oxidation,^{6,7} the water-gas shift reaction,^{8,9} the oxidation of alcohols,^{10,11} and epoxidation of propylene.^{12,13} In addition, high surface area nano-scale gold catalysts also promote hydrogenation of unsaturated chemical bonds (e.g., CO,¹⁴ CO₂,¹⁵ acyclic alkenes,^{16,17} cyclic alkenes,¹⁸ alkynes¹⁹ and derivatives of benzene²⁰⁻²²). Fundamental studies of gold catalysts regarding oxidation reactions are relatively abundant and this research has led to enhanced understanding of the related chemistry.²³⁻³⁷ However, insights into the mechanisms of hydrogenation reactions on gold model catalysts are lacking.

As the most stable and readily formed facet on classical catalysts, the Au(111) single crystal is a planar representative of gold-based catalysts. However, it is well known that gold has a high barrier for the dissociative adsorption of molecular hydrogen,³⁸ which necessitates employing H atoms to populate the surface in vacuum. While Sault, Madix and Campbell were able to adsorb hydrogen onto the Au(110) surface using a hot filament, there have been no investigations of the hydrogenation reactions on Au surfaces at low pressures.³⁹ Furthermore, there have been no experimental reports concerning adsorption and desorption of hydrogen or investigations of hydrogenation reactions on Au(111).

In this chapter, we report on our investigation of hydrogenation chemistry via H adatoms on Au(111) by employing acetaldehyde as a probe molecule. We show that H_2 and D_2 recombinatively desorb from the clean Au(111) surface with peaks for both between ~108 K and ~116 K, significantly lower temperatures than for Au(110), (216

K).39 We also demonstrate that the hydrogen covered Au(111) surface can mediate hydrogenation of acetaldehyde to ethanol at 180 K (or lower). Hydrogenation using adsorbed deuterium atoms results in a lower production of CH3CHDOD suggesting a primary kinetic isotope effect.

EXPERIMENTAL SECTION



Figure 2.1: Supersonic molecular beam scattering apparatus. The UHV system consists of a source section for generating molecular beam and a scattering section for TPD measurements and surface properties characterizations. Five separated subchambers are pumped differentially by diffusion and turbomolecular pump (P1-P5). A QMS is installed in the bottom part of subchamber 5 and the tower one is mounted by an AES, a LEED, an ion gun (IG), and a H doser. Crystal can be freely moved by a manipulator between beam level and instrumental tower. An inert flag (F1), shutters for both beams (S1, S2) and a mechanical chopper (CH) are also installed for controlling experiments on various purposes.

All experiments were conducted in a supersonic molecular beam apparatus under ultra high vacuum (UHV) conditions with a base pressure of 2×10^{-10} Torr. A detailed description has been reported previously.⁴⁰ Figure 2.1 shows a simplified schematic for this system. The beam source chambers (subchamber 1-3, respectively pumped by a Vrian VHS-6 diffusion pump, a Vrian VHS-4 diffusion pump, and a Vrian M-4 diffusion

pump. All these pumps are backed by a Welch 1376 mechanical pump) are differentially pumped and generate the reactant molecular beam. The auxiliary molecular beam (which was mainly used in this dissertation) of each of the reagents was introduced to the scattering chamber using a device consisting of separated nozzles, each with the same aperture size and separate plumbing to insure reagent purity as delivered to the sample. The scattering chamber (subchamber 5, pumped by a Vrian TV 551 Navigator turbomolecular pump) is installed with quadrupole mass spectrometer (QMS), low energy electron diffraction (LEED), and Auger electron spectrometer (AES) is used for analysis. Note that the subchamber 4 is pumped by a Vrian TV 301 Navigator turbomolecular pump. Both P4 and P5 are backed by a Welch 1397 mechanical pump.

The sample is a circular Au(111) single crystal with a diameter of 12 mm and a thickness of 2 mm, and firmly clamped by a molybdenum wire slotted in an edge groove for mounting on a pair of copper power leads, which allows the sample to be resistively heated to ~900 K with a proportional-integral-derivative controller and cooled to ~77 K by a liquid nitrogen bath. A K-type thermocouple (Alumel-Chromel) is embedded in a hole on the top edge of the Au(111) sample to measure the temperature.

H atoms were generated from a home-built hydrogen thermal cracker, by decomposing H₂ gas (MG Industries, 99.99 %) or D₂ (Praxair, 99.7 %) in a white-hot tungsten capillary (~ 2000 K) or exciting H₂/D₂ molecules [that can dissociate to H atoms upon striking the Au(111) surface]. The W capillary was heated by an electron beam emitted from a high-temperature tungsten filament with an acceleration voltage of 1 kV and an emission current of 20 mA. The H thermal cracker was constructed based on previous designs from other research groups.^{41,42} Since the efficiency of the H thermal cracker is unknown, in this work hydrogen/deuterium exposures were represented via the total amount of H/D (atoms and molecules) in Langmuir (L, 1 Langmuir = 1×10^{-6}

Torr·s) units. In addition, H/D relative coverages were determined by comparing TPD (temperature programmed desorption) spectra integrals to the integral for the saturated surface. We designate 1 monolayer (ML) of acetaldehyde (Acros Organics, extra pure 99.5 %) as the minimum coverage yielding the maximum integration area under the TPD spectrum excluding contributions from multilayer desorption (with peak temperature at ~115 K).

Routinely before every experiment, the Au(111) single crystal sample was cleaned by exposing to a NO₂ molecular beam with a flux rate ~ 0.1 ML/sec at 800 K for 2 minutes. The cleanliness of surface was verified by AES measurement. Periodically, contamination on the sample surface was removed by Ar^+ ion bombardment/sputtering. Subsequently, the sample was annealed at 800 K for 15 minutes and LEED was employed to examine the surface structure.

RESULTS AND DISCUSSION

Figure 2.2 displays H₂ and D₂ temperature programmed desorption (TPD) spectra from Au(111). Note that exposures of 50 L saturate the sample with H or D, thus we define a coverage relative to saturation $\theta_{H,rel}$ (or $\theta_{D,rel}$) for lower exposures as displayed in Figure 2.2 and referred to later. Hydrogen shows a desorption feature with peak temperatures in the range of 108-111 K in Figure 2.2a. This small range suggests that the peak temperatures are nearly constant indicative of first-order desorption kinetics although we expect second-order kinetics from the recombination of hydrogen atoms and subsequent desorption of H₂. It has been reported previously that the recombinative desorption rate of oxygen from Au(111) is first-order or zero-order as Koel *et al.*⁴³ and Gong *et al.*⁴⁴ observed for O adatom recombination on Au(111). Based on the Redhead approximation⁴⁵ using a frequency factor of 10¹³ s⁻¹ and desorption temperature of 110 K, the desorption activation energy of H₂ is estimated to be ~28 kJ/mol⁴⁶ [lower than that on Au(110), 51 \pm 4 kJ/mol³⁹] yielding a H-Au surface binding energy of ~ 231 kJ/mol, in good agreement with DFT calculations (214 kJ/mol).⁴⁷ Additionally, DFT calculations indicate that H atoms favor adsorption on 3-fold fcc hollow sites on the Au(111) surface.⁴⁷



Figure 2.2: H₂ (a) and D₂ (b) TPD spectra from Au(111) following adsorption of various relative coverages at 77 K. Coverages of hydrogen ($\theta_{H, rel}$) and deuterium ($\theta_{D, rel}$) are relative to the saturated surface. Note that (a) and (b) have the same scale on Y-axis. The heating rate was 1 K/s.

Figure 2.2b displays D_2 TPD spectra from clean Au(111) with desorption peaks centered between 111 - 116 K. This series of TPD spectra show desorption peaks very slightly increasing in temperature with higher deuterium coverages, again suggesting first-order desorption kinetics as with hydrogen (Figure 2.2a). The desorption activation energy of deuterium is ~ 30 kJ/mol⁴⁸ via the Redhead equation with a frequency factor of 10^{13} s⁻¹ and a desorption peak temperature of 114 K. Note that the desorption activation energy for deuterium is slightly higher than for hydrogen, in agreement with previous studies on other coinage metals (Cu^{49,50} and Ag⁵¹). For the same exposures, D₂ yields slightly smaller relative coverages than those from H₂ desorption from the Au(111) surface. We believe that this difference is likely due to the efficiency of our H/D thermal cracker for the different isotopes.

In order to study hydrogenation chemistry on Au(111), we co-adsorbed acetaldehyde on the H atom pre-covered surface at 77 K and subsequently annealed the sample at a ramp rate of 1 K/s. We expect near unity adsorption of acetaldehyde molecules using a neat molecular beam with kinetic energy ~ 9.6 kJ/mol^{52,53} for exposing both the clean and H/D-pre-covered Au(111) sample. Figure 2.3a shows the temperature programmed reaction of co-adsorbed acetaldehyde [0.35 ML (monolayer)] and hydrogen ($\theta_{H,rel} = 0.98$) on Au(111). Ethanol, produced by hydrogenation of acetaldehyde, begins desorbing at ~ 180 K and reaches a maximum at ~ 210 K. We also monitored the other characteristic mass fragments for ethanol by QMS including masses 45 and 46, which show a desorption peak at the same temperature as mass 31 confirming the production of ethanol. Note that molecularly adsorbed ethanol has two desorption features on the clean Au(111) surface; one at ~145 K attributed to multilayer desorption and the second at ~ 175 K due to monolayer desorption, as shown in Figure 2.4.⁵⁴



Figure 2.3: TPD of ethanol [(a) Mass 31 and (b) Mass 33] from 0.35 ML acetaldehyde adsorbed Au(111) with co-adsorption of a variety of relative coverages (exposures) of a) hydrogen and b) deuterium. Note that (a) and (b) have the same scale on Y-axis. All species were adsorbed on the surface at 77 K. The heating rate was 1 K/s.



Figure 2.4: Ethanol TPD (m/e = 31) from clean Au(111). We also monitored other mass fragments to confirm ethanol desorption. Ethanol was adsorbed on the surface at 77 K. The heating rate was 1 K/s.

Multiple control experiments have been performed as shown in Figure 2.5 in the supporting information, ensuring that ethanol can accurately be identified from mass 31 as due to the hydrogenation of CH₃CHO on Au(111) rather than from impurities from our H-atom doser and/or background contaminants. As shown in curve (*f*) of Figure 2.5, ethanol (mass 31) is produced and desorbs with a peak at ~ 210 K from co-adsorbed acetaldehyde [0.35 monolayers (ML)] and 25 Langmuirs (L) hydrogen, demonstrating the hydrogenation of acetaldehyde to ethanol on Au(111). In order to assure our conclusion, several blank experiments were conducted. We adsorbed 0.35 ML acetaldehyde on the clean Au(111) surface without hydrogen, and didn't observe the desorption of ethanol via mass 31 [see curve (*a*) in Figure 2.5], nor via mass 45 or 46. Hence, the ethanol detected in the reaction is not due to impurities of reactant acetaldehyde. When we power on our H atom doser, in general the pressure of the UHV chamber rises to 2×10^{-9} Torr from the base value of 2×10^{-10} Torr. We exposed the clean Au(111) sample to the H thermal cracker degassing for 50 seconds (equal to the time period for 25 L hydrogen exposure)

and then adsorbed acetaldehyde on the surface. No ethanol is detected as curve (b) shows, suggesting that degassed impurities are not responsible for the production of ethanol in the reaction. In addition, we exposed the sample to 25 L gas H₂ without supplying power to the H doser and subsequently co-adsorbed 0.35 ML acetaldehyde. As expected, TPD measurements don't yield CH₃CH₂OH production and display that no H₂ desorbs from the metal surface, indicating that the impurities in hydrogen cannot induce the production of species observed for mass 31 [see curve (c)]. We also exclusively exposed the single crystal to 25 L hydrogen and do TPD immediately without acetaldehyde on the surface. No ethanol is observed [see curve (d)], and it is further verified that ethanol is not due to either impurities of H₂ or degassing from the H doser operation. In order to examine if the reaction occurs on surfaces (such as copper power leads, copper connector, molybdenum sample-holding wire, and type-K thermal couple wire) other than Au(111), we backfilled 25 L hydrogen onto the sample, and then introduced acetaldehyde onto our inert stainless steel flag via molecular beam [instead of on the Au(111) surface] for 50 seconds [the same time period that we dose 0.35 ML CH_3CHO on the sample]. The subsequent TPD, as shown with curve (e), doesn't yield any production of ethanol indicative of the critical role for Au(111) in the hydrogenation reaction. By collecting all the information regarding blank experiments as described above, we believe it is appropriate to conclude that the H pre-covered Au(111) surface is active for acetaldehyde hydrogenation at a temperature below ~ 180 K.



Figure 2.5: TPD of ethanol from Au(111) following (a) 0.35 ML CH₃CHO adsorption, (b) 50s degassing of H thermal cracker (the same conditions to expose 25 L hydrogen except for feeding H₂ gas through the H thermal cracker to make H atoms/excited molecules) and 0.35 ML CH₃CHO adsorption, (c) 25 L H₂ exposure without operating the H thermal cracker and co-adsorption with 0.35 ML CH₃CHO, (d) 25 L hydrogen exposure, (e) 25 L hydrogen exposure and CH₃CHO impingement on the stainless steel inert flag (the same conditions to dose 0.35 ML CH₃CHO except for dosing on the sample), and (f) 0.35 ML CH₃CHO adsorption on the 25 L hydrogen precovered surface. Note that 25 L exposure of H can result in a relative coverage of 0.98 for H atoms on Au(111). All species were adsorbed on the Au(111) surface at 77 K. The heating rate was 1 K/s.

We examined the effect of varying hydrogen coverage with a fixed acetaldehyde coverage (0.35 ML of CH₃CHO). As shown in Figure 2.3a, increasing coverages of hydrogen promote higher production of ethanol [i.e., with increasing $\theta_{H,rel}$, the relative values of the integrated mass 31 (the -CH₂OH fragment of CH₃CH₂OH) signals in Figure 2.3a are 0.50, 0.80, 0.89, and 1.00, respectively]. We estimate that the acetaldehyde conversion is ~ 10 %, at most. A better estimate of the conversion is complicated by (i) a negligible (i.e., immeasurable) amount of acetaldehyde is consumed by reaction with atomic hydrogen and (ii) a calculation of the conversion based on the quantity of ethanol

produced involves significant uncertainty stemming from the different QMS ionization sensitivities and mass fragmentation ratios of ethanol and acetaldehyde and their pumping speeds.

Deuterium was also employed in the reaction in order to confirm our observations on the H pre-covered surface and achieve a better understanding of CH₃CHO hydrogenation kinetics on Au(111).⁵⁵⁻⁵⁷ As Figure 2.3b shows, a mass 33 signal (the – CHDOD fragment) is detected with a peak at ~ 210 K (similar to the mass 31 signal in the case of adsorbed hydrogen atoms), which is the largest mass fragment for CH₃CHDOD. This result and control experiments (not shown here) further confirm the production of ethanol via a reaction between H/D and acetaldehyde. Similar to the hydrogen pre-covered surface, increasing deuterium coverage results in more reacted acetaldehyde producing larger amounts of ethanol [i.e., with increasing deuterium coverage, the relative values of the integrals of the mass 33 (CH₃CHDOD) signals are 0.41, 0.58, 0.66, and 1.00 respectively in Figure 2.3b]. Clearly, as illustrated in Figure 2.3, more acetaldehyde can be hydrogenated on the H pre-covered surface than on the deuterated Au(111) surface (i.e., the integrated areas under mass 31 TPD spectra are greater than those under mass 33 signals). We estimate that the deuterium covered surface yields CH₃CHDOD with a production equivalent to roughly one-quarter that for CH₃CH₂OH formed with the hydrogen pre-covered surface under the same reaction conditions. In addition, during the hydrogenation reaction no H-D scrambling products (such as deuterated acetaldehydes) have been detected.



Figure 2.6: a) Selected TPD spectra of ethanol from 25 L hydrogen ($\theta_{H,rel} = 0.98$) precovered Au(111) with co-adsorption of a variety of amounts of acetaldehyde b) Ethanol production with varying CH₃CHO coverages on 25 L hydrogen pre-covered Au(111). All species were adsorbed on the surface at 77 K. The heating rate was 1 K/s.

The effect of acetaldehyde coverage as displayed in Figure 2.6a shows higher production of ethanol with increasing CH₃CHO coverage over the range from 0.1 to 1.27 ML (co-adsorbed with hydrogen at $\theta_{H,rel} = 0.98$). Figure 2.6b displays the relationship between ethanol production and acetaldehyde coverage which is linear at low CH₃CHO coverages. The production of ethanol plateaus when the CH₃CHO coverage reaches ~1 ML, and remains approximately constant with further increases in exposure, suggesting

that 1 monolayer of acetaldehyde can saturate the adsorption/active sites while further adsorption of CH₃CHO is incorporated into the multilayer and is not involved in the surface reaction with adsorbed H. The amount of H which desorbs during our temperature programmed reaction measurements is approximately equivalent to what would be measured without co-adsorbed acetaldehyde, further suggesting a relatively low reaction probability for acetaldehyde hydrogenation on Au(111). Similar results concerning D are shown in Figure 2.7 where larger amounts of acetaldehyde cause more ethanol to be formed on the deuterium co-adsorbed surface.



Figure 2.7: TPD of ethanol from 25 L a) hydrogen ($\theta_{H,rel} = 0.98$) and b) deuterium ($\theta_{D,,rel} = 0.83$) pre-covered Au(111) with co-adsorption of a variety of acetaldehyde coverages. All species were adsorbed on the surface at 77 K. The heating rate was 1 K/s.

To access mechanistic information about acetaldehyde hydrogenation on Au(111), we first investigated adsorption and desorption of acetaldehyde from the clean surface. Indeed, desorption of acetaldehyde from our clean Au(111) surface displays a

complicated spectrum as shown in Figure 2.8, showing two configurations $[\eta^{1}(O)]$ and $\eta^2(C,O)$] of adsorbed CH₃CHO and polyacetaldehyde (including the surface polymer in two dimensions and the polymer above the surface in three dimensions).^{58,59} In Figure 2.8, acetaldehyde shows a desorption feature at ~ 135 K with a low coverage (0.1 ML), which we ascribe to monolayer desorption as $\eta^1(O)$ CH₃CHO. With increasing coverages, a high temperature desorption feature appears with a broad peak in the range of ~ 200 -270 K. We speculate this feature is due to $\eta^2(C,O)$ CH₃CHO which is from the decomposition of two-dimensional polymerized acetaldehyde on the surface. For coverages higher than 1 ML (e.g., the black curve) a multilayer desorption peak at ~ 115 K appears. Note that a new feature at ~ 175 K is observed from 1.92 ML CH₃CHO adsorbed Au(111), which probably causes the formation of three-dimensional CH₃CHO polymer above the surface. Henderson *et al.* reported that multilayer CH₃CHO is crucial for the polymerization in three dimensions on Ru(001).⁵⁸ We speculate that the decomposition of bulk polymer evolves CH₃CHO with a peak at ~ 175 K from the surface with a heating rate of 1 K/s. After multilayer desorption, the strong moleculemolecule interaction results in the formation of clusters/islands from 3-D polyacetaldehyde on the surface, which coexists with monolayer CH₃CHO but leads to a comparably higher temperature desorption feature of CH₃CHO via the decomposition of polymer. In order to verify our speculations and identify CH₃CHO adsorption states on Au(111), further investigations are required with assistance of theoretical calculations and other surface techniques.



Figure 2.8: TPD spectra of acetaldehyde (m/e = 29) with varying coverages on Au(111) at 77 K. The heating rate was 1 K/s.



Figure 2.9: TPD spectra of acetaldehyde (m/e=29) and ethanol (m/e = 31) from Au(111) co-adsorbed by 0.35 ML CH₃CHO and 25 L H ($\theta_{H,rel}$ = 0.98) at 77 K. The heating rate was 1 K/s.

Interestingly, the desorption spectra undergo a complicated transformation when acetaldehyde is co-adsorbed with atomic hydrogen on Au(111), indicating a strong interaction between CH₃CHO and hydrogen on the surface. Notably, a new desorption feature for acetaldehyde occurs concomitantly with product ethanol desorption as shown in Figure 2.9 and leads us to speculate that an intermediate complex is created which decomposes to both CH₃CHO and CH₃CH₂OH beginning at ~ 180 K and reaching the highest reaction rate at ~ 210 K. We speculate that polyacetaldehyde species form on our Au(111) surface^{58,60} and are attacked by H/D adatoms to generate intermediate complexes (i.e., H/D modified 2-dimensional polyacetaldehyde) prior to complete H₂/D₂ desorption. The decomposition of the partially hydrogenated intermediate at 180 K likely leads to the prompt and simultaneous desorption of ethanol and acetaldehyde since this temperature is higher than either molecularly adsorbed CH₃CHO or CH₃CH₂OH (CH₃CHDOD) desorption from the clean Au(111) surface. The observation that CH₃CHDOD evolves at the same temperature as CH₃CH₂OH suggests that the barrier for decomposing the modified 2-D polymer is independent of the identity of the hydrogenating species (H or D). Thus, the lower reactivity of hydrogenation using D is a result of a lower probability of forming D-modified polymer in the first step of this reaction. These complicated mechanistic details are not currently fully understood and likely will require further study employing computational modeling and vibrational spectroscopy (these studies are underway). However, our primary message in chapter is adatom recombinative desorption and low-temperature to demonstrate H/D hydrogenation of acetaldehyde to ethanol.

CONCLUSIONS

Atomic hydrogen and deuterium were populated on the clean Au(111) surface at 77 K under UHV conditions with subsequent recombinative desorption upon annealing to yield desorption peaks in the range ~ 108 - 116 K with activation energies of ~ 28 kJ/mol (H) and ~ 30 kJ/mol (D), suggesting that H/D is very weakly bound to the Au(111) surface. Additionally, acetaldehyde is hydrogenated to ethanol on H/D pre-covered Au(111) at low temperature with a small conversion (10 % at most). Compared to hydrogen, deuterium shows a lower reactivity for the reaction with a smaller production of ethanol. We are hopeful that this study will yield insights into gold as a hydrogenation catalyst.

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Chapter 3: Chemoselective Hydrogenation of Acetone and Propionaldehyde

INTRODUCTION

The hydrogenation chemistry of oxygenated hydrocarbons has been studied on transition metal surfaces for a variety of reactions that are important to the pharmaceutical and chemical industries.^{1,2} For example, the chemoselective hydrogenation of α,β -unsaturated carbonyls (e.g., acrolein^{3,4} and crotonadehyde⁵) to produce unsaturated alcohols has attracted much attention. However, one of the primary concerns is that, theoretically, the C=C double bond is thermodynamically more likely to be hydrogenated than the C=O moiety.⁶ Many heterogeneous catalytic systems have been investigated searching for high selectivity in C=O bond hydrogenation.^{7,8}

In the past decades since nanoscale gold was found to be catalytically active,⁹⁻¹¹ gold-based catalysts have been studied theoretically^{12,13} and experimentally.¹⁴⁻¹⁸ These catalysts exhibit high reactivity in a wide range of reactions^{19,20} that include hydrogenation processes.^{2,21-23} Supported gold nanoparticles show great promise for the hydrogenation of unsaturated carbonyls to unsaturated alcohols.²⁴ Claus and coworkers found that in the production of allyl alcohol from acrolein hydrogenation, gold catalysts yield ~ 10 times higher selectivity for C=O bond hydrogenation than traditional platinum-based catalysts.²⁵ Their research indicates that the morphology of gold particles play a substantial role^{26,27} – the low-coordinated edges of the gold particles are active sites for the reaction.²⁴ However, fundamental studies of gold catalysis of C=O bond hydrogenation have not been performed.

Here we investigate acetone and propionaldehyde on a H pre-covered Au(111) surface as a model gold catalyst to examine the surface chemistry of C=O hydrogenation. H atoms were used in this study due to the high energetic barrier for H₂ dissociation.²⁸

Temperature programmed desorption (TPD) measurements indicate different activities for gold; propionaldehyde converts to 1-propanol on H-covered gold but acetone does not form 2-propanol. Density functional theory (DFT) calculations reveal dissimilar activation energies for the reactions between a single carbonyl moiety and H atoms.

EXPERIMENTAL SECTION

All experiments were conducted in an ultra-high-vacuum (UHV) supersonic molecular beam apparatus with a base pressure of 2×10^{-10} Torr. A detailed description has been reported in our previous publications^{29,30} and Chapter 2. This differentiallypumped system consists of a sub-chamber generating the molecular beam and a scattering chamber for analysis with installation of a quadrupole mass spectrometer (QMS), an Auger electron spectrometer (AES), and low energy electron diffraction (LEED) optics. We used a circular Au(111) single crystal with 12mm diameter and 2mm thickness, which is mounted on a pair of copper electrical feedthroughs and can be resistively heated to 900 K by a proportional-integral-differential (PID) controller and cooled to 77 K by a liquid nitrogen reservoir.

Prior to every experiment, the sample is routinely cleaned by exposure to a NO₂ molecular beam for 2 min while holding the surface temperature at 800 K.^{31,32} Periodically, we applied Ar ion sputtering to remove contaminants from the surface followed by annealing the sample at 800 K for 15 min. The surface structure and cleanliness are verified by LEED and AES.

H atoms were employed in this work, and are generated via a home-built device^{33,34} by introducing H₂ gas into a electron-beam heated tungsten tube to produce H atoms or excited hydrogen molecules that may dissociate to H adatoms once exposed to on the Au(111) surface. We quantify the coverage of H/D atoms as a relative coverage by

comparing to the TPD (temperature programmed desorption) from a H/D-saturated surface. The coverages of acetone and propionaldehyde were determined by comparing to the integration area of 1 ML species, which is designated as the amount of CH₃COCH₃ or CH₃CH₂CHO yielding a maximum integration area in the monolayer desorption feature.

All DFT calculations were performed within the Vienna *ab initio* Simulation Package (VASP).³⁵⁻³⁸ The PW91 GGA functional³⁹⁻⁴¹ was applied using the correlation interpolation scheme of Vosko *et al.*⁴² The single-electron Kohn-Sham orbitals for valence electrons were expanded in a plane-wave basis with an energetic cutoff of 274 eV and the core electrons were held frozen in the projector-augmented wave pseudopotential framework.^{43,44} The Brillouin zone of the 3x3 Au(111) slab was sampled with a 4x4x1 Monkhorst-Pack *k*-point mesh and a finite temperature smearing width of 0.2 eV in the Methfessel-Paxton scheme.^{45,46} The Au fcc lattice constants were set according to Wang *et al.*⁴⁷ For reaction rates, the climbing image nudged elastic band was used in order to find the saddle points.^{48,49} In all cases, atoms were allowed to relax until the maximum force per atom was less than 0.01 eV/Å.

RESULTS AND DISCUSSION

The hydrogenation of acetone was investigated on the Au(111) surface. In a control experiment, as illustrated by Figure 3.1a, 1.62 ML of acetone (m/z = 43, the most abundant mass fragment for acetone) was adsorbed on clean Au(111). Upon heating to 300 K with a ramp rate of 1 K/s, two desorption features appeared, which are attributed to second-layer desorption at 132 K and monolayer desorption at 155 K. With increasing acetone coverages, multilayer desorption creates a distinct feature at 126 - 131 K, as shown in Figure 3.2. Our TPD data is in excellent agreement with results from Koel *et*

 $al.^{50}$ Note that the signal from m/z = 58 (parent mass of acetone) was also monitored to verify desorption of CH₃COCH₃.



Figure 3.1: TPD spectra following adsorption of 1.62 ML of acetone (CH₃COCH₃) on a) clean and b) H pre-covered ($\theta_{H,rel} = 1$) Au(111). All species were adsorbed on the surface at 77 K. The heating rate was 1 K/s. Note that (a) and (b) have the same scale for the *Y*-axis.

On the H pre-covered Au(111) surface, the acetone thermal desorption spectrum shows a significant transformation as illustrated in Figure 3.1b. Compared to clean Au(111), H adatoms cause the desorption features to broaden. This interaction also slightly shifts the monolayer desorption to a higher temperature of 158 K and results in two new desorption features at 195 and 210 K. However, no hydrogenated products (e.g.,

2-propanol at m/z = 45) were observed. Further, no deuterated 2-propanol was generated from either H + CD₃COCD₃ or D + CH₃COCH₃. The experimental results clearly indicate that, while there is a noticeable interaction between acetone and hydrogen on the Au(111) surface, the catalytic activity is not high enough to initiate a reaction.



Figure 3.2: TPD spectra of acetone from Au(111) following the adsorption at 77 K.

In order to compare gold as a hydrogenation catalyst for aldehydes as compared to ketones, we investigated propionaldehyde hydrogenation. Figure 3.3 illustrates TPD measurements of propionaldehyde on a clean (Figure 3.3a) and H pre-covered (Figure 3.3b) Au(111) surface. As Figure 3.3a shows, 1.82 ML of propionaldehyde, represented by both m/z = 29 (-CH₃CH₂ and CHO) and 31 (-CH¹⁸O; from natural abundance of ¹⁸O), yields multilayer and monolayer desorption features at 121 and 154 K, respectively. We also observed another desorption feature at 269 K, which is likely associated with the polymerization of CH₃CH₂CHO on the clean surface. The polymerization of aldehydes has been widely reported on many metal surfaces including Ru,⁵¹ Au,⁵² Cu,⁵³ and Pd.⁵⁴

More detailed information for propionaldehyde desorption with varying coverages is provided in Figure 3.4.



Figure 3.3: TPD spectra following adsorption of 1.82 ML of propionaldehyde (CH₃CH₂CHO) on (a) the clean surface and (b) atomic hydrogen ($\theta_{H,rel} = 1$) pre-covered Au(111). All species were adsorbed on the surface at 77 K. The heating rate was 1 K/s. Note that (a) and (b) have the same scale for the *Y*-axis.



Figure 3.4: TPD spectra following adsorption of 1.82 ML of propionaldehyde (CH₃CH₂CHO) on (a) the clean surface and (b) atomic hydrogen ($\theta_{H,rel} = 1$) pre-covered Au(111). All species were adsorbed on the surface at 77 K. The heating rate was 1 K/s. Note that (a) and (b) have the same scale for the *Y*-axis.

With H co-adsorption, the TPD desorption spectra for propionaldehyde shows several changes. Figure 3.3b shows a TPD measurement following the co-adsorption of 1.82 ML of CH₃CH₂CHO and H adatoms ($\theta_{H,rel} = 1$) on Au(111) at 77 K. The desorption spectrum of m/z = 29 clearly indicates that the multilayer and monolayer desorption features shift to higher temperatures (147 and 186 K, respectively). In addition, the multilayer desorption yields a smaller peak, whereas the monolayer desorption feature remains at 271 K with a smaller integrated area. These changes are likely due to an interaction between CH₃CH₂CHO and H that further facilitates the hydrogenation of CH₃CH₂CHO and produces 1-propanol. The desorption peak at 220 K for the m/z = 31 curve in Figure 3.3b indicates that 1-propanol is formed. The other features for m/z = 31 are due to propionaldehyde desorption [~ 3 % of m/z = 29 as in Figure 3.3a]. We estimate that 90 % of the desorption peak at ~ 220 K (at m/z = 31) can be assigned to 1-propanol. The production of $CH_3CH_2CH_2OH$ has been affirmed by the parent mass fragment peak of 1propanol at m/z = 60 with the same shape and temperature as shown in Figure 3.5.



Figure 3.5: TPD spectra following 1.86 ML of adsorption of propional dehyde on atomic hydrogen ($\theta_{H,rel} = 1$) pre-covered Au(111) following the adsorption at 77 K.

The comparison between reactions of acetone and propionaldehyde with H reveals a higher reactivity of CH_3CH_2CHO on Au(111) and suggests chemoselectivity in the hydrogenation chemistry of the gold surface. We employed DFT calculations in order to understand the mechanisms at a molecular/atomic scale, similar to the study performed by Alcala and co-workers on a model Pt(111) surface.⁵⁵ They found that the hydrogenation of propionaldehyde is more favorable due to its lower activation energy (0.54 eV) compared to acetone (0.76 eV). They assert that protonation of the carbonyl

carbon is the first step, which is followed by the hydrogenation of the oxygen.⁵⁵ However, our DFT calculations in Figure 3.6 show different reaction pathways and mechanisms on gold.



Figure 3.6: Energy diagram for acetone and propionaldehyde hydrogenation on Au(111).

Acetone and propionaldehyde are structural isomers of one another. Due to the thermodynamic stability of ketones compared to aldehydes, acetone is calculated to be 0.33 eV lower in energy than propionaldehyde in the gas phase. Neither of these two molecules display a significant binding to the Au(111) surface; each binds with an energy of ~ 0.1 eV. The key step that anchors the molecules to the surface is the protonation of the carbonyl oxygen. In each case, this process has a barrier of 0.2 eV. Following
protonation, the carbonyl carbon becomes sp^3 hybridized and forms a covalent bond with a surface gold atom. This process is shown graphically in Figure 3.6, which shows the displacement of the gold atom out of the surface due to the covalent interaction (panels 2A and 2B). Due to the increased sterics of the bulky methyl groups at the alpha carbon positions in acetone, this protonation step is only exothermic by 0.1 eV. In contrast, protonated propionaldehyde suffers less steric interaction with the surface and the protonation step is exothermic by over 0.4 eV.



Energy Landscape

Figure 3.7: Energy diagram of polymerization of acetone and propionaldehyde on Au(111) and mediated by an excess proton.

Following the initial protonation of the carbonyl oxygen, the carbonyl carbon is vulnerable to attack by surface hydrogen atoms. Although this reaction is highly exothermic in both cases, Figure 3.6 clearly explains the observance of 1-propanol and not 2-propanol. The barrier to protonate the carbonyl carbon in propionaldehyde is significantly lower than the barrier to return the proton to the surface. In contrast, acetone

has a lower barrier and low energetic cost of returning the initial proton to the surface. It is more favorable to reform acetone from the protonated version than it is to protonate the carbonyl carbon in terms of reaction barriers. With increasing temperature during the TPD measurements, 1-propanol formation is favored simply by following the lowest reaction barriers. In contrast, the lowest reaction barriers favor desorbing acetone.

An additional factor that favors propionaldehyde hydrogenation is the polymerization reaction. A comparison of Figures 3.1a and 3.3a shows that propionaldehdye polymerizes on the clean surface but acetone does not. Similar phenomena also occur on H covered Au(111). Following protonation of the carbonyl oxygen, the carbon becomes activated. As shown in Figure 3.7, polymerization with a second surface molecule is exothermic by 0.45 eV in propionaldehyde and is endothermic by 0.3 eV in acetone. Thus, these polymerization reactions help to account for the increased susceptibility to hydrogenation of propionaldehyde. The more strongly bound polymer desorbs at a much higher temperature, so the concentration of surface molecules is higher at increased temperature such that the polymer may dissociate and undergo full hydrogenation. This is also consistent with our observation in Figure 3.3b that propionaldehyde shows a concomitant desorption feature with produced 1-propanol at 220 K, which has also been observed in acetaldehyde hydrogenation on Au(111).⁵² Acetone, in contrast, does not polymerize, so desorption from the surface remains favored as compared to hydrogenation.

As shown in Figure 3.3b, we also observed the desorption of di-n-propyl ether $(CH_3CH_2CH_2OCH_2CH_2CH_3)$ from propionaldehyde on H covered Au(111). This species is represented by the m/z = 73 curve with a desorption feature centered at 225 K, which is verified by two other characteristic mass fragments at m/z = 43 and 102 as shown in Figure 3.5. Mass 43 is the most abundant fragment and mass 102 is the parent mass.

Figure 3.3a shows that the di-n-propyl is not from impurities in the reactant and strongly suggests that the compound is formed via a coupling reaction of propionaldehyde. We note that water desorption was observed at 180 K and further indicates ether synthesis via a mechanism akin to the standard acid-catalyzed dehydration reaction in solution. A more detailed study is underway regarding the related reaction mechanisms.

Isotopic experiments were performed in order to further investigate reaction mechanisms. We studied the hydrogenation between CH₃CH₂CHO and D atoms as shown in Figure 3.8a, where 1.86 of ML propionaldehyde was adsorbed on deuterated Au(111) ($\theta_{D,rel} = 1$). The TPD spectrum for m/z = 33 displays a peak at 220 K, the same temperature as the desorption of 1-propanol in Figure 3.3b, and indicates CH₃CH₂CHDOD production, which is verified by detection of the corresponding parent mass of 62 (not shown). Additionally, we detected partially deuterated di-n-propyl ether (CH₃CH₂CHDOCHDCH₂CH₃) with the characteristic mass fragment 75 and a desorption peak at 225 K. The desorption peak of the mass fragment 44 and the parent mass 104 are also observed (not shown).

In addition, these isotopic experiments provide insight into the kinetic isotope effect (KIE) on the surface reactions. Figure 3.8b shows the integrated areas under the desorption features of products 1-propanol (m/z = 31 and 33) and di-n-propyl ether (m/z = 73 and 75) as the indicator of their corresponding productions in H- and D-involved reaction systems. The results indicate lower reactivity of deuterium for the surface reactions and show ratios of 2.9 for mass 31/mass 33 (indicating production of 1-propanol) and 1.3 for mass 73/75 (indicating production of the ether). Thus, we conclude that the reaction between propionaldehyde and H adatoms is influenced by a KIE, which is comparably stronger for the hydrogenation of propionaldehyde than the formation of di-n-propyl ether.



Figure 3.8: (a) TPD spectra following adsorption of 1.82 ML of propionaldehyde (CH3CH2CHO) on atomic deuterium (θD,rel = 1) pre-covered Au(111). (b) Production of 1-propanol and di-n-propyl ether from the H and D covered surface. All species were adsorbed on the surface at 77 K. The heating rate was 1 K/s.

CONCLUSIONS

In summary, acetone has a weak interaction with atomic H on Au(111) as indicated by TPD desorption spectra compared with acetone on clean Au(111). No hydrogenated product, however, has been observed. In contrast, the hydrogenation of propionaldehyde is detected via the production of 1-propanol. DFT calculations predict similar energetic barriers for the initial protonation reaction; however, the reverse of this reaction is favored in acetone as compared to the final hydrogenation step. Thus, the full hydrogenation is favored in propionaldehyde as compared to any reverse reaction. In addition, the polymerization of CH_3CH_2CHO on Au(111) is exothermic and may play a role in the hydrogenation reaction by increasing the surface concentration of propionaldehyde. Di-n-propyl ether can be generated via a coupling reaction of propionaldehyde on H covered Au(111) and is likely due to the reaction between surface intermediates and the produced alcohol. Deuterium shows lowered reactivity for the production of both 1-propanol and di-n-propyl ether and indicates a kinetic isotope effect.

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Chapter 4: Tunable Ether Synthesis via Coupling of Aldehydes or Aldehyde/Alcohol

INTRODUCTION

Supported gold-based catalysts have been identified with high activity for many oxidative processes.¹⁻¹⁰ In addition, a number of hydrogenation reactions on supported gold nanoparticles have also been studied,¹¹⁻¹³ showing particularly great promise for selective hydrogenation.¹⁴⁻¹⁶ However, related fundamental studies with model gold catalysis are lacking and highly desired in order to achieve an enhanced understanding of reaction mechanisms. Part of this gap is due to a high energetic barrier for hydrogen to dissociatively adsorb on gold surfaces,¹⁷ requiring population of atomic hydrogen on the surface¹⁸ to simulate hydrogen dissociation as with classical catalysts.^{19,20} These weakly chemisorbed H atoms show exceptional reactivity and are, for example, able to hydrogenate acetaldehyde to ethanol at ~ 200 K.²¹

Ethers are an important class of organic compounds which are widely utilized as solvents, starting materials for polymers, fine chemicals and pharmaceuticals.^{22,23} Currently, the most prevailing methods for ether synthesis are (1) the reaction of alcohols and mineral acids (Scheme 4.1A), and (2) the Williamson ether synthesis, for symmetrical and unsymmetrical ethers, respectively (Scheme 4.1B).²⁴ However, the first method operates at harsh conditions (strong acids and high temperature) and often leads to undesired chemistry, such as acid-mediated dehydration to give olefins; the second one requires use of toxic and expensive alkyl halides as starting materials. In addition, although significant progress has been made in the preparation of more complex ether products with homogeneous catalysis,²⁵⁻²⁸ limited success has been achieved using heterogeneous processes. Milone and co-workers reported the only heterogeneous process involving gold as a catalyst: they produced cinnamyl ethyl ether and 2-

ethoxyprop-1-enylbenzene via cinnamaldehyde hydrogenation on Au/TiO₂ heterogeneous catalysts at 333 K.²⁹ However, no follow-up work has been reported to date.



Scheme 4.1: Ether synthesis.

In this chapter, using weakly bound H atoms, we conduct our study of hydrogenation chemistry on a Au(111) single crystal sample, a planar representative of classical gold catalysts. We observe the formation of diethyl ether and di-n-propyl ether from H pre-covered Au(111) with co-adsorption of acetaldehyde and propionaldehyde, respectively. Low H coverage increases the selectivity of ether formation over alcohols. Further, when co-adsorbing different aldehydes or alcohols-aldehydes on H/Au(111), the corresponding unsymmetrical ethers can be generated on the surface. We propose mechanisms involving a reductive coupling reaction of surface species for ether synthesis in which partial hydrogenation of the aldehyde to form an alcohol-like intermediate is a key step.

EXPERIMENTAL SECTION

All experiments were conducted in an ultra-high-vacuum (UHV) supersonic molecular beam apparatus with a base pressure of 2×10^{-10} Torr. A detailed description

has been reported in our previous publications^{30,31} and Chapter 2. A circular Au(111) single crystal was employed as a catalysts, which can be resistively heated to 900 K by a proportional-integral-differential (PID) controller and cooled to 77 K by a liquid nitrogen reservoir A quadrupole mass spectrometer (QMS) was used to monitor the gas phase species desorbing from the smaple surface.

The sample is cleaned by exposure to a NO_2 molecular beam for 2 min while holding the surface temperature at 800 K.^{32,33} Periodically, Ar ion sputtering is utilized to remove contaminants from the surface, after which the sample must annealed at 800 K for 15 min.

Au(111) by itself is unable to dissociate and adsorb molecular hydrogen at low temperatures. In order to adsorb hydrogen atoms onto the surface, H₂ gas was introduced into a custom-built electron-beam heated tungsten tube^{34,35}, which produced either H atoms or excited hydrogen molecules that dissociate to H adatoms once exposed to the Au(111) surface. After H atoms are adsorbed onto the surface, the reactants are then deposited by the molecular beam apparatus described above. The coverage of H/D atoms is quantified by comparing the integrated area of the TPD desorption peak to that of the surface saturated with H/D. Similarly, the coverages of reactants (acetaldehyde, propionaldehyde, methanol, thanol, 1-propanol, diethyl ether, and di-n-propyl ether) were determined by comparing the peak integration area of a characteristic mass fragment to that of 1 ML of reactant, which is designated as the amount of reactant yielding a maximum integration area in the monolayer desorption feature without the presence of a multilayer desorption feature.

RESULTS AND DISCUSSION



Figure 4.1: a) TPD spectra following adsorption of 0.65 ML of acetaldehyde on H ($\theta_{H,rel}$ = 0.74) pre-covered Au(111). b) Production and selectivity (*S*) of diethyl ether and ethanol. All species were adsorbed on the surface at 77 K. The heating rate was 1 K/s.

We first investigate the formation of diethyl ether. Figure 4.1a displays the temperature programmed desorption (TPD) spectra from 0.65 ML of CH₃CHO and H ($\theta_{H,rel} = 0.74$) co-adsorbed on Au(111). Acetaldehyde (0.65 ML) yields two desorption features on the clean surface, corresponding to monolayer desorption and surface polymerization peaks at ~ 135 K and ~ 240 K, respectively.²¹ In contrast, on the H covered surface, as shown in Figure 4.1a, the desorption of acetaldehyde (at m/z = 29,

indicative of –CHO) shows a complicated transformation: the monolayer peak shifts to ~160 K, a new feature is apparent at ~ 210 K, and no polymerization feature is observed. These changes indicate a strong interaction between CH₃CHO and H mediated by the Au(111) surface inducing hydrogenation of acetaldehyde to ethanol, indicated by a desorption feature at ~ 210 K of two characteristic ethanol mass fragments in QMS, m/z = 31 and m/z = 46.



Figure 4.2: TPD spectra of diethyl ether from Au(111), following adsorption at 77 K. The heating rate was 1 K/s.

In this TPD measurement as shown in Figure 4.1a, the formation of diethyl ether has also been observed from a self-coupling reaction of CH₃CHO with assistance of H adatoms on Au(111). The produced (CH₃CH₂)₂O is indicated by the m/z = 59 and 74 signals (for the -CH₂OCH₂CH₃ group and the parent ion, respectively), initially desorbing from the surface at ~175 K and reaching a peak value at ~ 190 K. Note that on clean Au(111), diethyl ether desorbs at a lower temperature (peak at ~ 175 K – Figure 4.2). Thus, desorption of surface reaction produced (CH₃CH₂)₂O is a reaction-limited process. Water, another product, is also detected with a desorption feature starting at ~ 175 K, higher than the characteristic desorption of water on the clean surface (starting at 140 K and peaking at ~ 155 K³⁶). Thus, the overall surface reaction is likely: 2 CH₃CHO + 2 H \rightarrow (CH₃CH₂)₂O + H₂O. Furthermore, a control experiment with acetaldehyde on clean Au(111) indicated no ethanol or diethyl ether production (see Figure 4.3), confirming the hydrogenation reactions on the surface.



Figure 4.3: TPD spectra of acetaldehyde from Au(111), following adsorption at 77 K. The heating rate was 1 K/s.

Based on the TPD measurements, it is clear that there are two reaction channels between acetaldehyde and H atoms on the surface, yielding ethanol and diethyl ether, respectively. Accordingly, we have investigated production and selectivity for those two products with varying H coverages. Figure 4.1b indicates that with decreasing H coverages from 1.0 to 0.1, the production of both ethanol and diethyl ether decreases. Note that our measurements have limits to accurately determine the product yields and reactant conversions due to species-dependent pumping speeds and uncertainties in coverages. However, we estimate the yield of the ether and ethanol to be ~ 10 %, at most. In addition, plot (b) indicates that the selectivity for the ether increases with decreasing surface H atoms despite the lower production at low H coverages. Additionally, we examined co-adsorbed ethanol and H on Au(111) for synthesizing diethyl ether but no such species was produced. Combined, these results indicate that not only is acetaldehyde an essential reactant, but that ether production and alcohol production are somewhat competing reactions, mediated by H coverage. We speculate that the ether formation is, therefore, likely associated with a coupling reaction between reactant acetaldehyde and a surface intermediate generated from partial hydrogenation of CH₃CHO, which will be discussed in detail later. A low coverage of H increases the likelihood of this interaction before full conversion of CH₃CHO to CH₃CHO to CH₃CHO can occur, leading to the enhancement of ether production.

Similarly, H adatoms can hydrogenate propionaldehyde to 1-propanol and cause a self-coupling reaction to produce di-n-propyl ether on the Au(111) surface, as shown in Figure 4.4. The production of 1-propanol can be confirmed by the detection of two characteristic mass fragments, m/z = 31 and 60. Di-n-propyl ether (m/z = 73 for – CH₂OCH₂CH₂CH₃ and m/z = 102 for parent ion) also forms during the reaction showing a desorption feature across ~ 210 – 270 K peaking at ~ 240 K. This desorption feature occurs at higher temperatures compared to (CH₃CH₂CH₂)₂O on clean Au(111) surface, as shown in Figure 4.5 again suggesting a reaction-limited desorption process. Moreover, water is produced at the relatively high temperature of ~ 175 K. In addition, Figure 4.4b indicates that increasing H coverages can promote the formation of CH₃CH₂CH₂OH and (CH₃CH₂CH₂)₂O while suppressing the selectivity for di-n-propyl ether, similar to acetaldehyde on H/Au(111) as discussed previously. In Figure 4.6, a control experiment with propionaldehyde on the clean Au(111) surface, is provided to support our

observations of the formation of propanol and di-n-propyl ether in the presence of H atoms.



Figure 4.4: a) TPD spectra following adsorption of 0.70 ML of propionaldehyde on H $(\theta_{H,rel} = 0.74)$ pre-covered Au(111). b) Production of selectivity of di-n-propyl ether and 1-propanol. All species were adsorbed on the surface at 77 K. The heating rate was 1 K/s.



Figure 4.5: TPD spectra of di-n-propyl ether from Au(111), following adsorption at 77 K. The heating rate was 1 K/s.



Figure 4.6: TPD spectra of propionaldehyde from Au(111), following adsorption at 77 K. The heating rate was 1 K/s.



Figure 4.7: TPD spectra of produced ethers from the aldehdyes and alcohols coadsorbed Au(111) surface which is pre-covered by H atoms with a relative coverage of 0.74 ($\theta_{H,rel} = 0.74$). All species were adsorbed on the surface at 77 K. The heating rate was 1 K/s.

Figures 4.1 and 4.4 indicate a self-coupling reaction of aldehydes to generate symmetrical ethers. We also investigated the syntheses of unsymmetrical ethers via the coupling reaction between different aldehydes or alcohols-aldehydes. Figure 4.7 illustrates the formation of a variety of unsymmetrical ethers from the corresponding aldehydes and alcohols. For example, on the H-covered Au(111) surface, methyl ethyl ether (at m/z = 60) and methyl propyl ether (at m/z = 74) can be observed from coupling reactions of methanol/acetaldehyde and methanol/propionaldehyde, respectively. Furthermore, ethyl propyl ether can be synthesized by a coupling reaction via either ethanol/propionaldehyde or 1-propanol/acetaldehyde. Note that ethyl propyl ether can

also be produced from the reaction of two different aldehdyes, acetaldehyde and proionaldehyde. Interestingly, the $CH_3CH_2OCH_2CH_2CH_3$ produced via three different chemical reactions yields a desorption feature starting at the same temperature, ~ 190 K, in all three cases. Those reactions, as illustrated in Figure 4.7, suggest a new method for the synthesis of unsymmetrical ethers by tuning the reactant alcohols and aldehydes correspondingly. However, it should be noted that symmetrical ethers are also produced from the self-coupling of aldehydes (e.g., diethyl ether is detected due to CH_3CHO self-coupling during the synthesis of $CH_3CH_2OCH_3$ and $CH_3CH_2OCH_2CH_2CH_3$). In this case, more studies are needed to further investigate the selectivity towards symmetrical and unsymmetrical ethers by adjusting concentrations of reactant feeds. Figure 4.8 shows that co-adsorbed aldehydes and alcohols are unable to generate ethers without H co-adsorption.



Figure 4.8: TPD spectra of multiple ethers from Au(111) with co-adsorption of different aldehydes and alcohols at 77 K without coadsorption with hydrogen atoms. The heating rate was 1 K/s.

Based on the above, mechanisms for these processes are proposed (Figure 4.9, Path 1 for aldehyde/aldehyde coupling; Path 2 for alcohol/aldehyde coupling). Adsorption and desorption of aldehydes have been studied on various metals, such as Ru,³⁷ Au,²¹ and Pd.³⁸ On clean surfaces, aldehydes favor the $\eta^1(O)$ configuration in which the carbonyl oxygen interacts with the surface via a lone pair. Previous DFT calculations have predicted that H atoms on Au(111) favor hydrogenating the oxygen of the aldehyde first, with a small energy barrier of ~ 0.25 eV, resulting in an alcohol-like surface intermediate, R-HC(OH)-Au(111) (see step b in path 1).³⁹ We believe this partially hydrogenated intermediate is crucial for further coupling with aldehydes. This hypothesis is supported by: 1) alcohols (fully hydrogenated products from aldehydes) alone cannot form ethers on H/Au(111); 2) aldehydes on the clean surface cannot yield ethers (Figures 4.3 and 4.6); 3) no ether is formed on Au(111) with co-adsorption of only aldehydes and alcohols (Figure 4.8 – i.e., no coadsorbed H); and (4) a negative correlation between hydrogen coverage and ether selectivity is observed (Figures 1b and 4b). These results clearly indicate that both H and aldehyde are indispensable for ether formation, and partial hydrogenation of aldehydes is a key step. In path 1, note that water is generated as a by-product during ether formation. In addition, we detected the production of $(CH_3CHD)_2O$ and $(CH_3CH2CHD)_2O$ during the process of syntheses of diethyl ether and di-n-propyl ether on D-covered Au(111). This confirms one of the proposed elementary steps - the addition of surface H atoms to the α -carbon in aldehydes.

The proposed alcohol/aldehyde reaction mechanism (Path 2) is similar to the aldehyde/aldehyde mechanism (Path 1), except that the α -carbon hydrogenation step of the second aldehyde reactant is not required, whereas dissociation of the alcohol O-H bond is. The other work in our group regarding ethanol-hydrogen interactions on Au(111) shows that this O-H bond dissociation is indeed observed for alcohols on hydrogen pre-covered Au(111). Following the partial hydrogenation of the aldehyde (step b), this dissociation allows the alcohol-aldehyde coupling interaction, shown in step c, to then occur. Subsequent steps are similar to path 1 - water and ether are produced in steps d and e, respectively, with the Au surface providing stabilization when a bond on the α -carbon is broken. In addition, since the O-H bond is ~ 10 cal/mol stronger than the C-H bond, we cannot conclusively rule out mechanisms involving a C-H dissociation step, as is illustrated in Figure 4.10. In this process, the alcohol R'-CH₂-OH is converted to the surface intermediate via a H-exchange reaction with an aldehyde-induced intermediate.



Figure 4.9: Schematic diagram of proposed mechanisms for ether synthesis on H/Au(111). Path 1 demonstrates the production of ether from aldehydes coupling. Path 2 indicates the coupling reaction between alcohols and aldehydes. When R' = R, the product is symmetrical ether. Otherwise, unsymmetrical ether is produced.



Figure 4.10: Schematic diagram of ether production mechanisms via an alcohol-aldehdye coupling reaction including C-H bond cleavage in alcohols (step c).

CONCLUSIONS

In this chapter, we report a method for ether synthesis from simple aldehydes and alcohols mediated by H-covered gold. Acetaldehyde and propionaldehyde are homocoupled on H/Au(111) to produce symmetrical ethers. Further, we observe that coupling reactions between aldehydes and alcohols can generate corresponding unsymmetrical ethers, which can also be synthesized via coupling of mixed aldehydes. We propose a mechanism, in which an alcohol-like intermediate, formed by partial hydrogenation of an aldehyde, plays a key role. This reaction allows us to control molecular structures of synthesized ethers by selecting corresponding aldehydes and alcohols, revealing the remarkable surface chemistry of gold in hydrogenation processes. Future work could include translation of this discovery to heterogeneous gold catalysis for preparing various ethers from a broader range of aldehydes and alcohols.

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Chapter 5: Interaction of Atomic Hydrogen with Water

INTRODUCTION

High activity has been found on nanoscale gold-based catalysts for a variety of chemical transformations^{1,2} at low-temperatures including selective hydrogenation reactions.^{3,4} However, relevant fundamental, model studies of catalytic hydrogenation chemistry over gold are severely lacking. Model investigations⁵ could provide valuable insights into the reaction mechanisms and catalytic properties of gold^{6,7} and help advance the state of the art. Although there is a large energetic barrier to H₂ dissociation on pristine gold surfaces,^{8,9} it is clear that the metal oxide-gold interface can readily dissociate hydrogen¹⁰ and hydrogen spillover onto the gold results in a very weakly bound H atom^{9,11} that is quite reactive, leading to the high hydrogenation activity observed at low-temperatures in classical catalysis experiments.

Here, we further demonstrate the remarkable surface chemistry of gold^{12,13} via a study involving adsorbed H/D atoms which activate the dissociation of water on a Au(111) sample. Pt surfaces have also shown hydrogenic isotopic exchange via an interaction between adsorbed hydrogen and water,¹⁴⁻¹⁷ however, here the Au(111) surface reveals new details regarding the structure of the hydrogen-water overlayer on the surface. Since water and hydrogen are prevalent in the chemistry and physics of many processes,^{18,19} we believe that our studies will be of utility regarding: 1) gold catalyzed chemical reactions involving H and H₂O, such as the water gas shift reaction,^{20,21} and steam reforming of hydrocarbons²² and alcohols;²³ 2) applications of gold electrodes in aqueous solutions;²⁴ and 3) the formation of hydronium (H₃O⁺)²⁵ and protonated water clusters [(H₂O)_nH⁺]²⁶ that are associated with proton transfer and transport in water and which have been studied widely in many fields of chemistry and biology.²⁷

It is well known that water adsorbs intact on Au(111) and has a small binding energy with the surface.^{28,29} However, in the present work we observe that co-adsorbing H atoms and water molecules on Au(111) reveals newly formed desorption features for both species in temperature programmed desorption measurements that indicate stronger interactions. Employing an isotopically-labeled reaction system, such as $D_2O + H$ or H_2O + D, we have discovered the production of scrambled H₂, HD and D₂. Our results suggest a reaction of water with H adatoms on Au(111), and further identify the origins of H (from surface H atoms or H₂O molecules) for each H₂ desorption feature in the H + H₂O system. Density functional theory (DFT) calculations are employed to understand the mechanisms - clusters of water play a key role in the reaction with H atoms on the surface. Formation of protonated water (H₂O)_nH⁺ as an intermediate is energetically favorable and its thermodynamics and structure account for the non-random H-D exchange in H-D₂O and D-H₂O systems.

EXPERIMENTAL SECTION

We employed an ultrahigh vacuum (UHV) supersonic molecular beam apparatus for all experiments that has a base pressure of ~ 1×10^{-10} Torr.^{30,31} The detailed description has been reported previously³² and Chapter 2. This system includes a differentially-pumped chamber for molecular beam generation and an analysis chamber with a quadrupole mass spectrometer (QMS), an Auger electron spectrometer (AES), and low energy electron diffraction (LEED) optics. The model catalyst sample is a single crystal Au(111) disk, which can be resistively heated to 900 K employing a proportionalintegral-differential (PID) controller and cooled to 77 K via a liquid N₂ bath. Vibrational spectroscopy measurements were conducted in another UHV chamber which is installed with a Fourier transform infrared spectrometer and a mercury–cadmium–telluride detector (MCT).³³ A multi-nozzle assembly was employed with a single set of beam defining apertures to create molecular beams of water vapor (and NO₂ for sample cleaning) that completely covered one face of the sample.

We cleaned the sample surface via a 2 min exposure to a NO_2 beam with the sample held at 800 K before every experiment.^{34,35} Periodically, we employed Ar ion sputtering to remove contamination from the surface followed by annealing the sample to 800 K for 15 min. The cleanliness and surface structure of the sample was routinely verified by AES and LEED.

H/D atoms were generated via a homemade device, in which gas-phase hydrogen/deuterium was introduced into an electron-beam heated high-temperature tungsten capillary tube to produce H/D atoms or excited molecules that dissociate to atoms once adsorbed to the sample surface.¹¹ The hydrogen coverage is represented as a relative coverage in comparison with the hydrogen-saturated surface. The water coverage is designated based on the beam flux rate with 0.067 ML/sec which was calibrated on an Ir(111) surface.^{31,36}

All DFT calculations were performed within the Vienna ab initio Simulation Package using the PW91 GGA functional.³⁷⁻⁴¹ Kohn-Sham orbitals were expanded in a plane wave basis with an energetic cutoff of 274 eV.⁴² Core electrons were held frozen within the projector-augmented wave framework.^{43,44} The Brillouin zone was sampled with a 4x4x1 Monkhorst-Pack k-point mesh and Methfessel-Paxton finite temperature smearing with a width of 0.2 eV.^{45,46} The Au lattice constant was taken from Wang *et al.*⁴⁷ Barriers were determined using the climbing-image nudged elastic band method.^{48,49}

RESULTS AND DISCUSSION



Figure 5.1: TPD spectra from Au(111) with (a) adsorption of only 2.68 ML H₂O and (b) adsorption of only H ($\theta_{H,rel} = 0.74$) and (c) co-adsorption of 2.68 ML H₂O and H ($\theta_{H,rel} = 0.74$). All species were adsorbed on the surface at 77 K. The heating rate during TPD was 1 K/s. Note that (a), (b) and (c) have the same *Y*-axis scale.

Figure 5.1 displays our first indications of the intricate interactions between adsorbed hydrogen and water on gold. At the outset it is perhaps instructive to examine the TPD spectra for adsorbed H and H_2O independently as shown in Figures 5.1a and b in order to better appreciate the interactions revealed for the co-adsorbed system. Figure

5.1a displays TPD spectra for H_2O from the clean Au(111) surface at a heating rate of 1 K/s. Water desorption has only a single feature on clean Au(111) at 157 K²⁸ as is shown in Figure 5.1a. Recombinative hydrogen desorption from Au(111) also shows a single feature, peaking at 110 K, as is displayed in Figure 5.1b.

Now turning our attention to TPD spectra regarding the H and H₂O co-adsorbed surface as shown in panel c of Figure 5.1, the measurements exhibit three H₂ desorption features that are denoted as α , β , and γ and are centered at 136 K, 158 K, and 175 K, respectively. The α peak is assigned to H atoms recombining but with a higher temperature compared to characteristic H₂ desorption (~ 110 K) from the clean surface as illustrated in Figure 5.1b.¹¹ The other two desorption peaks (β , γ) are newly formed and clearly involve the co-adsorbed water. Based on the integrated TPD area under each peak, we estimate the proportion of the three features to be 83.5 %, 2.8 %, and 14.3 %, respectively for the α , β , and γ peaks.

Similarly, water desorption is also strongly affected by adsorbed hydrogen as shown in Figure 5.1c with a new feature appearing at a higher temperature, ~175 K, aligned with the γ peak in H₂ desorption. It should also be noted that the β peak from H₂ desorption reproducibly appears at a slightly higher temperature (158 K) than the primary water desorption peak at ~ 157 K as illustrated in Figures 5.1a and c.

In order to better understand the interaction between water and hydrogen on Au(111), we employed isotopes in the form of deuterium atoms and/or deuterated water to further probe reaction pathways. Figure 5.2 shows TPD spectra for two different experiments: a) H ($\theta_{H,rel} = 0.74$) pre-covered Au(111) with co-adsorption of 2.68 ML D₂O and b) D ($\theta_{D,rel} = 0.63$) pre-covered Au(111) with co-adsorption of 2.68 ML H₂O. Figure 5.2a indicates that the replacement of D₂O for H₂O on H pre-covered Au(111) still produces the two features α and β from H₂ desorption, but the γ desorption features for H₂

is missing at ~175 K. Instead, two desorption features have been observed, respectively, in mass 3 (HD) and mass 4 (D₂) in the temperature range near 175 K; this observation suggests a scrambling reaction between D₂O and H adatoms that induces the production of HD and D₂ on the Au(111) surface. This finding further indicates that the γ feature in the H₂ thermal desorption spectrum in Figure 5.1c stems exclusively from a hydrogenexchange reaction between H and H₂O rather than the recombination of originally adsorbed H atoms. We notice that the desorption of HD and D₂ in Figure 5.2a yields similar integrated areas, further indicating that ~ 75 % of the hydrogen in the γ peak in Figure 5.1c is from water. This finding suggests that the yield of exchanged H atoms on the surface is ~ 10.7 % (the γ peak is estimated to contribute 14.3 % of H₂ desorption in Figure 5.1c). However, HD and D₂ have slightly different ionization sensitivities in QMS measurements (leading to some uncertainty here).

In contrast, D_2O desorption shows two features at 160 and 180 K, similar to the observations for H and H₂O co-adsorbed on Au(111). The new feature for D₂O at 180 K, is at a slightly higher temperature than the similar one from H₂O desorption (175 K), and this feature is likely due to an isotope effect in which the H+D₂O system generates HD and D₂ via breaking the original O-D bond in D₂O as discussed in detail later. The mass 19 signal during TPD represents HDO, which can also be observed in D₂O desorption on clean Au(111) and is identified as an impurity. Stronger mass 19 signals have been observed at 160 K during TPD from the H/D₂O covered surface; this result is indicative of the production of HDO. This newly formed HDO desorbs at the same temperature as water desorption on clean Au(111), and we believe this isotopic mixing is due to proton transfer in the solid water film.⁵⁰



Figure 5.2: (a) TPD spectra from Au(111) with co-adsorption of 2.68 ML D₂O and H $(\theta_{H,rel} = 0.74)$, and (b) 2.68 ML H₂O and D $(\theta_{D,rel} = 0.63)$. All species were adsorbed on the surface at 77 K. The heating rate during TPD was 1 K/s. Note that (a) and (b) have the same scale in the *Y*-axis.

We also studied the Au(111) surface with co-adsorbed deuterium and H₂O. Figure 5.2b shows TPD spectra acquired from 2.68 ML H₂O adsorbed on D ($\theta_{D,rel} = 0.63$) precovered Au(111). There are significant similarities with the H-D₂O system shown in Figure 5.2a: *i*) H₂O shows a higher temperature desorption feature at 175 K; *ii*) D₂ yields a sharp desorption peak at 160 K; *iii*) the production of HD and H₂ has been observed, and the H₂ desorption peak appears at the highest temperature; *iv*) compared to the surface with adsorbed water (H_2O) only, there is an increase in mass 19 (HDO) at 160 K which is indicative of deuterium transfer in H_2O on Au(111).



Energy Landscape

Figure 5.3: Schematic mechanism of the diffusion of an H atom on Au(111). H atoms adsorb preferentially in the fcc hollow sites. With an energy barrier of ~0.30 eV, H atoms are able to move onto a top site.

We conducted density functional theory (DFT) calculations to uncover the detailed mechanism of the interaction of adsorbed H atoms with water (procedural details are contained in the supplemental information). The TPD spectra presented in Figures 5.1 and 5.2 indicate a specific reaction mechanism: isotopic mixing dictated via overlayer structure. The high temperature H₂ peak, γ in Figure 5.1, originates exclusively from the water; however, the two lower temperature H₂ peaks are derived exclusively from the surface-bound atoms. The fact that these sources of these peaks are related for both surface D/H₂O as well as surface H/D₂O indicates that this effect cannot be ascribed entirely to random isotopic scrambling.



Figure 5.4: Schematic mechanism of recombination and desorption of H atoms on Au(111) which are barrierless and exothermic by over 0.75 eV.

We first used DFT to model the behavior of surface-bound H at low temperatures. The three-fold fcc hollow sites are the most favorable adsorption sites for H atoms, as Mavrikakis has reported previously.⁵¹ As shown in Figure 5.3, there is a small barrier for a hydrogen atom to move from an fcc hollow to an hcp hollow. In this manner, the surface bound atoms may diffuse randomly across the surface at low temperatures. H₂ formation as well as interaction with water, however, requires H atoms to sit atop a surface Au atom. From this position, the reaction for two adjacent top-bound H atoms to form H₂ is barrierless and exothermic by over 0.75 eV (Figure 5.4). Thus, the formation of H₂ is not apparent until the temperature is such that the surface-bound protons may diffuse to top sites. This barrier, approximately 0.25 eV from a hcp hollow, represents the energy cost of extracting a surface-bound H-atom from the Au(111) surface, and all related processes, such as H₂ formation or the interaction with water have similar barriers.

In contrast, water is weakly chemisorbed on Au(111) and has little barrier to diffusion. Thus, multiple water molecules move around on the surface until clustering and stabilizing. This phenomenon has been demonstrated by the low surface wettability

of Au(111),¹⁸ which is a hydrophobic surface and induces the formation of water clusters with a double-bilayer structure.⁵² Specifically, water molecules have much stronger H₂O-H₂O interactions than H₂O-surface interactions on Au(111),¹⁸ causing a single desorption feature. On other metal surfaces (such as Ir,⁵³ Pt,⁵⁴ Ni,⁵⁵ etc.), there is a discernable transition from the monolayer to the multilayer desorption indicating a stronger interaction between the first layer of water and the surface atoms.



Figure 5.5: Schematic energy diagram of the interaction of atomic H with a water molecule or a dimer on Au(111). The interaction of atomic H with a single water molecule (a) is endothermic. In contrast, the newly formed bond between a surface H atom (b) and water dimer is strongly exothermic and the in-network bond lengthens.
Our DFT calculations for the H_2O + fcc-site H reaction show a 0.29 eV energetic barrier with a 0.22 eV exothermicity. The final H_3O^+ state has three fully equivalent protons and a low barrier for the reverse reaction, so if this reaction were to occur at low temperatures, random isotopic scrambling would occur. The lack of low-temperature scrambling of surface-bound H with water indicates that water molecules form ice before the energetic barrier for surface-bound H to escape the surface can be met. Note that the formation of hydronium has been reported on the H and water covered Pt(111) surface by Wagner and co-workers, who detected an H_3O^+ intermediate based on the appearance of a 1150 cm⁻¹ loss in high resolution electron energy loss spectroscopy (HREELS).⁵⁶

We next studied the interaction of H atoms with water dimers and clusters employing DFT. Protonated water clusters of the form $(H_2O)_nH^+$ are likely to form due to the strong exothermicity of the product state and a large barrier to the reverse reaction. DFT calculations investigated the protonation of a water dimer and a water tetramer as a representative of a water cluster. Protonation of the dimer is exothermic by 0.27 eV compared to the fcc hollow. Importantly, the H-bonded proton of the dimer becomes shared between the two molecules with an equal bond length, as shown in Figure 5.5. It is this stretching mechanism that allows the original water molecule to dissociate; when the dimer breaks apart at higher temperatures, it is the H atom that is originally part of the water molecule that creates the H₂ desorption observed at 175 K in Figure 5.1c.



Figure 5.6: Schematic energy diagram of the interaction of atomic H with water cluster on Au(111). When atomic H atoms from the surface adsorb to the edge of a water cluster, the interaction is strongly exothermic. Due to the favorable energetics of $(H_2O)_nH^+$ clusters as compared to H_3O^+ , when this cluster breaks apart, the original water molecule at the edge dissociates instead of returning the H atom to the surface or create H_3O^+ .

When a water tetramer is considered, protonation of the central water molecule is exothermic by 0.93 eV as compared to the fcc hollow as shown in Figure 5.6. Thus, when surface-bound H atoms become free to move about the surface, they can either recombine to form H₂ or encounter an under-coordinated water molecule at the edge of an ice cluster and bind irreversibly. Infrared spectroscopy provides evidence for this process. Figure 5.7 shows that the O-D bond stretch $(2425 \text{ cm}^{-1})^{18}$ is observed from the D and H₂O covered Au(111) surface upon heating the sample to 110 K and suggests that protonated water is formed. Over the same range of temperatures, D₂ recombinatively desorbs from the surface (Figure 5.2b), suggesting that D₂ desorption is a competing process with D-H exchange in the D+H₂O system and could further affect the protonation of water clusters. Note that when only the tetramer is considered as shown in Figure 5.6, all three of the edge water molecules surrounding the center H_3O -like species are equivalent and equally likely to desorb upon heating. However, for a larger cluster, the other two molecules in the tetramer could be considered as H-bonded to other H_2O molecules in the cluster, so they would be frozen and unable to leave. Thus, with increased heat applied during TPD, newly formed water molecules—now containing an originally surface-bound atom located at the edge of the cluster are the most energetically favorable portion to dissociate as the protonated ice cluster breaks apart. The energetic cost of putting the excess proton on the surface or on a single molecule is significantly larger than leaving the excess proton on a cluster of water molecules. In this manner, the edge water molecules dissociate and isotopic scrambling with surface H(D) occurs.



Figure 5.7: RAIRS (reflection absorption infrared spectroscopy) spectra from a) 6 ML H_2O and D ($\theta_{D,rel} = 1$) co-adsorbed Au(111) and b) 6 ML H_2O covered Au(111). H_2O was impinged onto H/Au(111) at 77 K via molecular beam following by incremental heating to each temperature. The sample is cooled to 77 K before collecting each spectrum.

In TPD measurements of co-adsorbed H and H₂O, recombinative H₂ desorption shows two new features (β , γ), and water desorption reveals an additional peak at higher temperature. DFT results show that the (H₂O)_nH⁺ clusters require a higher energy input to break up than (H₂O)_n and lead to the new high temperature desorption feature of water at 175 K. Each water cluster breaks apart into progressively smaller units and the ultimate effect of the breakup involves cleavage of an O-H (or O-D) bond that was originally part of a water molecule. The H (or D) atom in this bond is ultimately left on the surface as an adatom that can recombine with other H or D on the surface. In experiments involving isotopes, as illustrated in Figure 5.2, this process can produce scrambled HD and D₂/H₂ (in the H-D₂O/D-H₂O systems).

Thus, our DFT calculations demonstrate the origins of the α , β , and γ peaks. The α peak arises from the surface-bound H atoms that are free to diffuse on the surface and recombine. The hydrophobic Au(111) surface^{57,58} may induce water clustering upon heating, opening up more water-free surface area and increasing the ability of two H adatoms to recombine. However, ultimately, the water clusters lengthen the H atom diffusion distance, leading to the shift in the α peak to higher temperatures with increasing water coverage as shown in Figure 5.8. The β peak is the result of surface-bound H whose diffusion is obstructed by large ice clusters and which are not free to recombine until the water clusters begin to break apart at higher temperatures. More specifically, we speculate that the β peak is likely due to a physicochemical process: *i*) water adsorbs on the H pre-covered surface and forms clusters covering the H atoms; *iii*) the water cluster bottom, which is fully coordinated to other H₂O molecules, has a weaker interaction with H atoms than the edge water molecules; *iiii*) this interaction inhibits the mobility of H atoms; *iv*) H atoms combine with one another and immediately leave the Au(111) surface once water desorbs at ~ 160 K, leading to a slightly high desorption

temperature due to the reaction kinetics. The final peak, γ , consists of protons exclusively from the water and originate from surface-bound H atoms bonding with water molecules at the edges of ice layers to form (H₂O)_nH⁺ clusters that do not break apart until 175 K. This mechanism is consistent with the isotopic results presented in Figure 5.2, in which isotopic scrambling occurs based on the origin of the species—from the surface or from water. In addition, Figure 5.8 shows that increasing water coverages cause greater desorption features of H₂O and H₂ at 175 K, suggesting that more water clusters form at high coverages and generate a larger number of edge sites to promote the interaction between H and water. These results are in agreement with our DFT calculations that water clustering plays a key role in this process.



Figure 5.8: TPD spectra of (a) H₂ and (b) H₂O from H ($\theta_{H,rel} = 0.74$) pre-covered Au(111) with co-adsorption of a variety of H₂O coverages. All species were adsorbed on the surface at 77 K. The heating rate during TPD was 1 K/s. Note that (a) and (b) have the same scale in *Y*-axis.



Figure 5.9: (a) TPD spectra from Au(111) with co-adsorption of co-adsorption of 2.68 ML D₂O and D ($\theta_{D,rel} = 0.63$). (b) Integrated TPD areas from H₂ desorption at 175 K in H+H₂O and D₂ (also including HD and H₂) desorption at 180 K in D+D₂O. All species were adsorbed on the surface at 77 K. The heating rate during TPD was 1 K/s. Note that (a) and (b) have the same scale in *Y*-axis.

Kinetic isotope effects (KIE) have been studied by comparing co-adsorption of H and H₂O to a fully deuterated reaction system. 2.68 ML D₂O and D ($\theta_{D,rel} = 0.63$) co-adsorbed on Au(111) yields TPD spectra, shown in Figure 5.9a, that show several characteristic properties of the interaction between hydrogen and water. The D₂ desorption contains three features corresponding to the peaks α , β , and γ in Figure 5.9a,

and D_2O similarly shows a new high-temperature desorption feature. We also observed desorption of HD (mass 3) and H₂ (mass 2) in a temperature range of 175 – 180 K. These features likely result from the surface-mediated interaction between H-D₂O or D-H₂O, since D₂O and D₂ have a considerable amount of HDO (19 %) and HD (7 %) impurities, respectively, as indicated by multiple control experiments via TPD and FTIR measurements.

In order to identify the effect of deuterium on the reaction between hydrogen and water, we integrated the desorption features of D₂, HD and H₂ that peak at 175-180 K and show the results in Figure 5.9b with a comparison to the reaction of H with H₂O. Note that we normalized the difference between H and D coverages by assuming a proportional relationship between coverages and areas under the γ feature in H₂/D₂ desorption. The integrated areas indicate that with the interaction between H and H₂O generates a significantly larger amount of H₂ than the desorption of D₂ from the D-D₂O reaction by a factor of ~ 4. This result suggests a primary kinetic isotope effect for this surface reaction. In addition, we note that the sum D₂, HD and H₂ from D-D₂O is still smaller than H₂ desorption in the case of H+H₂O, as shown in Figure 5.1c. This observation is a further demonstration of the KIE influence, which is likely due to the elementary steps of water protonation and subsequent decomposition of (H₂O)_nH⁺.

CONCLUSIONS

In summary, hydrogen and water have a strong interaction that results in nonrandom isotopic scrambling on the Au(111) surface at low temperature (<175 K) under UHV conditions. Co-adsorbed H and H₂O lead to a new feature appearing at ~175 K in the water desorption spectra, which is in contrast to the characteristic desorption peak on clean Au(111) at 160 K. Furthermore, two new features have been observed in H₂ desorption (at 165 K and 175 K), as well as a shift in the characteristic H₂ recombination desorption feature to higher temperatures. We used two reactant combinations, H₂O + D and D₂O + H, to study these phenomena and show production of HD, HDO and H₂(D₂) via a mixing reaction based on the overlayer structure of isotopically labeled water and hydrogen. This study provides evidence that the hydrogen evolving at 175 K from the H and H₂O co-adsorbed surface is exclusively from bond-breaking in water rather than surface bound H₂ recombinative desorption. RAIRS spectroscopy and DFT calculations predict that protonated water clusters (H₂O)_nH⁺ are intermediates, which dissociate at higher temperature to cause the appearance of new desorption features for water and H₂. Purely deuterated reactants D and D₂O have been employed in this reaction and show a lower reactivity, indicative of a primary kinetic isotope effect.

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Chapter 6: Highly Selective and Facile NO₂ Reduction to NO

INTRODUCTION

The removal of NO_x (mainly NO₂ and NO) originating from automobile and power plant emissions is of importance as an environmentally benign technology.¹⁻³ Many studies have been conducted in the search for high-efficiency and low-cost catalyst formulations for NO_x reduction. However, there are inherent limitations in current processes such as a high activation energy for NO decomposition, selection of reducing agents (hydrocarbons cause a narrow reaction temperature window; urea/ammonia increases system complexity),^{4,5} and more stringent emission limit regulations.^{4,6} Thus, a fundamental understanding of NO_x reduction and the development of an effective catalyst are urgently needed

Gold-based catalysts have been studied for a wide range of energy-efficient processes⁷⁻¹⁸ as well as for hydrogenation chemistry.¹⁹⁻²⁷ NO_x reduction is also a potential application for gold catalysts and has been briefly investigated with H₂,^{28,29} propene,³⁰ or CO^{31,32} as reducing agents, but the mechanisms are not well understood. Here, we report a mechanistic study of NO₂ reduction to NO by atomic hydrogen using a model gold catalyst. The experimental results indicate that NO₂ can be converted to NO on H/Au(111) at a cryogenic temperature, 77 K. Unexpectedly high NO₂ conversion (100 %) and NO selectivity (100 %) are observed at temperatures lower than 120 K suggesting a highly selective and facile NO₂ reduction process mediated by the gold surface. Our previous work shows that atomic H has a small desorption activation energy of ~0.29 eV on Au(111),^{33,34} so these weakly chemisorbed hydrogen adatoms likely play a key role in facilitating such unique hydrogenation chemistry. Density functional theory (DFT) calculations and reflection-absorption infrared spectroscopy (RAIRS) measurements

provide insights into the relevant reaction mechanisms in which surface-bound HNO_2 and N_2O_3 are intermediates.

In this work, we employ a Au(111) single crystal as the model catalyst which can be considered as a planar representative of supported gold nanoparticles. In addition, since molecular hydrogen has a high energetic barrier to dissociation on model gold surfaces,^{35,36} we employ gas-phase H atoms to populate the surface so that hydrogenation chemistry can be studied. We hope that our study will assist in identifying the role of gold on classical supported catalysts where H₂ dissociates on the periphery sites and likely spills over onto the gold particles.³⁷ Although this work only yields NO₂ reduction to NO, high conversion of NO₂ and high selectivity to NO have been observed, indicating unique surface chemistry for gold and providing insights into its catalytic activity in hydrogenation reactions.

EXPERIMENTAL SECTION

All experiments were conducted in a supersonic molecular beam apparatus under ultra high vacuum conditions with a base pressure of 2×10^{-10} Torr.³⁸⁻⁴¹ More detailed information has been demonstrated in Chapter 2. The differentially pumped chamber consists of a source chamber to generate molecular beams and a scattering chamber for analysis, which contains a quadrupole mass spectrometer (QMS), an Auger electron spectrometer (AES), and low energy electron diffraction (LEED) optics. A circular gold sample is installed on a pair of copper power leads which can be cooled to 77 K by a liquid nitrogen reservoir and resistively heated to 900 K by a proportional–integral–derivative (PID) controller. A K-type thermocouple was applied to measure sample temperatures. Prior to every experiment, the sample was cleaned by exposing to an intense NO₂ molecular beam with the surface held at 800 K for 2 minutes.^{42,43}

Periodically, contamination on the sample was removed by Ar⁺ ion bombardment. The sample cleanliness and surface structure were verified by AES and LEED. IR measurements were carried out in another UHV chamber which has a Fourier transform infrared infrared spectrometer and a mercury–cadmium–telluride detector (MCT).⁴⁴

We employed a home-built device to generate H atoms via an electron-beamheated high temperature tungsten capillary in which molecular hydrogen is converted to H atoms or vibrationally excited molecules which dissociate on Au(111) at 77 K.^{45,46} The relative coverage of hydrogen and deuterium atoms is determined by comparing to the saturated surface. In order to avoid NO₂ decomposition and purity degradation, the gas handling system, including valves and tubes, was passivated by exposing to a relatively high pressure of NO₂ for a prolonged time. NO₂ was delivered onto the Au(111) surface via a molecular beam initiating from a device with an array of nozzles, each with the same aperture size and separate plumbing to insure reagent purity as delivered to the sample. The coverage of NO₂ is determined based on TPD spectra from Au(111), where 1 ML nitrogen dioxide is considered as the amount yielding a maximum integrated area under the monolayer desorption feature. Water was introduced onto the sample surface in a molecular beam with a flux rate of 0.067 ML/sec.^{41,47}

The calculations reported herein were performed on the basis of spin polarized density functional theory (DFT) within the generalized gradient approximation (GGA-PW91⁴⁸), as implemented in the Vienna Ab-initio Simulation Package (VASP).⁴⁹ The projector augmented wave (PAW) method with a planewave basis set was employed to describe the interaction between core and valence electrons.⁵⁰ An energy cutoff of 350 eV was applied for the planewave expansion of the electronic eigenfunctions. For the Brillouin zone integration, we used a (4×4×1) Monkhorst-Pack mesh of k points to calculate geometries and total energies. Reaction pathways and barriers were determined

using the nudged elastic band method (NEBM) with eight intermediate images for each elementary step.⁵¹ For Au model surfaces, we constructed a four atomic-layer slab with a hexagonal 3×3 unit cell. The slab is separated from its periodic images in the vertical direction by a vacuum space corresponding to seven atomic layers. The lattice constant for bulk Au is predicted to be 4.18Å, close to the experimental value of 4.08Å. While the bottom two layers of the four-layer slab were fixed at corresponding bulk positions, the upper two layers were fully relaxed using the conjugate gradient method until residual forces on all the constituent atoms became smaller than 5×10^{-2} eV/Å.

RESULTS AND DISCUSSION

We first performed molecular beam reactive scattering (MBRS) experiments to investigate the reduction of NO₂ on gold. A molecular beam-blocking shutter can be rapidly moved out/in of the path of the beam allowing/stopping the impingement of NO₂ molecules (the beam flux rate is 0.1 monolayer/sec with a kinetic energy of ~ 0.1 eV) on the Au(111) surface. A quadrupole mass spectrometer (QMS) was used to identify gasphase species reacting/scattering from the sample. Figure 6.1 displays QMS signals from species evolving from the sample during the 20 seconds of NO₂ (2.0 ML) impingement onto both clean and H ($\theta_{H,rel} = 1$) pre-adsorbed Au(111) at a surface temperature of 77 K. Panel (a) illustrates a control experiment: here NO₂ was impinged onto the clean Au(111) surface [without pre-covering the gold with H atoms] at *t* = 0 s where NO₂ molecules both adsorb and scatter off the sample and cause the QMS intensity increase observed. As the NO₂ beam strikes the surface over the entire 20 second experiment, a constant intensity for scattered NO₂, is observed suggesting that scattering/adsorption of NO₂ dominates this process (with no hint of reaction).



Figure 6.1: Molecular beam reactive scattering of NO₂. The beam strikes onto (a) the clean Au(111) surface (b) the H (relative coverage $\theta_{H,rel} = 1$) atom precovered Au(111) surface at 77 K. The NO₂ beam was impinged on the surface from 0 s to 20 s. The points denoted (*i*)-(*v*) mark specific times corresponding to measurements discussed later. The NO₂ beam flux is 0.1 ML/sec. Note that (a) and (b) have the same *Y*-axis scale.

With the Au(111) surface covered by H atoms at unity relative coverage (determined by comparing to a H-saturated sample surface), the MBRS experiments were performed with results shown in Figure 6.1b, indicating the evolution of NO from the surface at 77 K. Note that the sticking probability of NO₂ is ~ 60% on H-covered Au(111). In the initial ~ 4-5 seconds of impingement by the NO₂ beam, the NO signal shows virtually identical behavior to the experiment on clean Au(111) as shown in Figure 6.1a, suggesting an induction period. From t = 5 to 15 s, the signal for NO shows a significant evolution lasting for approximately 10 s and reaching a peak value at t = 10 s, demonstrating a reaction between adsorbed NO₂ and H adatoms. The points labeled from

(*i*)-(*v*) indicate various experimental stages including (*i*) beam on, (*ii*) the beginning, (*iii*) the peak, (*iv*) the end of NO evolution, and (*v*) beam off, respectively, which are discussed later with regard to relevant temperature programmed desorption (TPD) measurements, DFT calculations, and RAIRS studies. In contrast to NO, the NO₂ signal behaves similarly as in the control experiment, with a constant intensity. We also observe that the MBRS experiment results in H₂ evolution at 77 K. This phenomenon is also likely related to NO₂ reduction, which activates H atoms and induces the desorption of H₂ at low temperature.



20s (2.0 ML) NO₂/Au(111), T_s = 77 K

Figure 6.2: The unaltered data for the NO₂ MBRS experiments illustrated in Figure 6.1.

Note that both gaseous NO_2 and NO give signals for mass 30 in our mass spectrometer. For NO_2 , the signal for mass 30 arises from the gas-phase dissociation (into

NO and O) of the molecule in the electron bombardment ionization process whereas for NO mass 30 is the parent mass. Thus, the MBRS spectra for NO in Figure 6.1 have been modified by subtracting the mass 30 component due to NO_2 from the signals at mass 30 in order to provide a better description of the NO evolution during NO_2 impingement on H/Au(111). The unaltered data are shown in Figure 6.2.

To further explore the mechanistic details of this reaction, we conducted TPD measurements as a function of NO₂ coverage on the H-pre-covered ($\theta_{H,rel} = 1$) Au(111) surface at 77 K. The various NO₂ coverages are correlated to impingement times of the NO₂ beam and various stages of the reaction [i.e., points (*i*)-(*v*) displayed in Figure 6.1b]. Figure 6.3a and b display TPD spectra for masses 30, 46 and 18, respectively corresponding to NO+NO₂, NO₂, and H₂O, evolving from Au(111) upon heating the sample surface from 77 K to 300 K at a ramp rate of 1 K/s. The black curves are acquired from a control experiment with unity relative H coverage on Au(111) but zero coverage of NO₂ (corresponding to point (*i*) in Figure 6.1b), in which, as expected, no desorption products for masses 30, 46, or 18 are observed.

Next we studied the H/Au(111) surface ($\theta_{H,rel} = 1$) co-adsorbed with 0.5 ML of NO₂ [this is equivalent to 5 sec of NO₂ impingement and reaches the point at which the evolution of NO begins; i.e., point (*ii*) in Figure 6.1]. There is no desorption feature observed from the TPD spectrum for mass 46 indicating that the adsorbed NO₂ has completely reacted with the H adatoms yielding a 100% conversion. The TPD spectrum for mass 30 in Figure 6.3a shows a desorption feature with a peak at ~ 120 K, which can be completely attributed to desorbing NO rather than a mass fragment of NO₂ [since no mass 46 desorbs]. During the measurement, no other reduced products such as N₂O, N₂, or NH₃ were detected indicative of a high selectivity (100 %) towards NO.



Figure 6.3: TPD studies from NO₂ and H co-adsorbed Au(111). TPD spectra of mass 30, 46, and 18 after various coverages of NO₂ impingement to Au(111) with pre-adsorption of hydrogen atoms (relative coverage $\theta_{H,rel} = 1$) at 77 K. Note that (a) and (b) have the same scale for the *Y*-axis.

TPD measurements from the H-pre-covered ($\theta_{H,rel} = 1$) Au(111) surface after 10 s of NO₂ impingement were performed as shown in Figure 6.3a. This exposure of NO₂

results in a coverage of 1.0 ML and produces the maximum in NO evolution in MBRS [point *(iii)* in Figure 6.1b]. In the TPD measurements shown in Figure 6.3, the sample was heated to 300 K inducing a single broad feature from ~ 190 - 260 K in the spectrum for mass 46 indicative of NO₂ monolayer desorption, which is also apparent in mass 30 as the ionized fragment of NO₂. However, a significant desorption feature for mass 30 also appears with a peak at ~ 120 K. This feature is not duplicated in mass 46 and clearly suggests NO₂ reduction on the surface with subsequent NO desorption.

Point (iv) in Figure 6.1b indicates that the evolution of NO nearly vanishes after 15 s of NO₂ impingement (1.5 ML) on the H pre-covered Au(111) surface. On a comparably covered surface, the TPD experiment produces two desorption features with similar shape for both mass 30 and 46 (Figure 6.3a), in which peak temperatures are consistent with the distinct desorption features of NO_2 from clean Au(111).⁵² Thus, we infer that the mass 30 signal is primarily (but not exclusively) from NO₂ fragmentation with little parent NO. Note that with decreasing H surface concentration [no detection of H_2 desorption at point (*iv*) indicating that H atoms are completely consumed] and a constant NO₂ beam flux, a portion of the NO₂ molecules directly adsorb on Au(111) without reacting and also contribute to the desorption features we measure in Figure 6.3a. We estimate that the evolved NO after point (*iv*), as shown in Figure 6.1b, is from ~ 6.1 % of the total NO₂ molecules that have absorbed on the surface during 15 s of NO₂ beam impingement. Further extending the NO₂ impingement time until 20 sec [point (v) in Figure 6.1b] results in a larger desorption feature for NO₂ in mass 30 and 46 at ~ 130 K as shown in Figure 6.3a, when the surface reactions are ending and NO_2 is beginning to populate the multilayer on Au(111).

Figure 6.3b displays TPD spectra for water produced from the surface reaction between H adatoms and adsorbed NO₂ molecules on Au(111). The black curve illustrates

a control experiment indicating, as expected, no water formation on the solely H-covered surface. With increasing NO₂ coverage on the H-precovered surface, water desorption sequentially yields for point *(ii)* a single peak at ~ 150 K [consistent with the characteristic desorption peak of water on clean Au(111)⁵³], for *(iii)* a single peak at ~ 190 K, and for *(iv)* and *(v)* two features apparent at both ~ 160 K and ~ 190 K. This water desorption behavior is likely related to the progress of reaction involving H adatoms and NO₂ as well as their concentrations on the surface and will be discussed more later.

Reaction	$\theta_{\rm H} \sim 1 \; (\theta_{\rm E} \sim 0)$		$\theta_{\rm H} \sim 0 \; (\theta_{\rm E} \sim 1)$	
	$\Delta E (\mathrm{eV})$	$E_{\rm a}({\rm eV})$	$\Delta E (\mathrm{eV})$	$E_{\rm a}({\rm eV})$
<i>i</i>) - <i>ii</i>) Induction				
$NO_2(g) \rightarrow NO_2$	-0.30		-0.81	
$NO_2 + H \rightarrow H_{dw}ONO$	-1.13	0.04	-0.45	0.55
$H_{dw}ONO \rightarrow H_{up}ONO$	-0.02	0.28	-0.24	0.35
<i>ii) - iv)</i> NO evolution				
$\rm H + H_{up}ONO \rightarrow$	-0.72	0.47	-0.90	0.30
$NO + H_2O$	-0.72	0.47	-0.90	0.50
$NO + NO_2 \rightarrow N_2O_3$			-0.03	0.27
<i>iv) - v)</i> Post-evolution				
$NO_2(g) \rightarrow NO_2$			-0.81	

 Table 6.1:
 Energetics/barriers of surface reactions during molecular beam reactive scattering experiments

The results of our density functional theory (DFT) calculations are summarized in Table 6.1 for which two types of surfaces have been compared regarding the H adatom coverage on Au(111) (here a low hydrogen coverage, θ_{H} , corresponds to more empty sites, represented by θ_{E}). Figure 6.4 shows a representative energy diagram for NO₂ reduction and NO evolution on Au(111) at $\theta_{H} = 1$, illustrating species adsorption and transition states. It should be noted that the geometric configurations of molecules and intermediates on the surface are independent of surface H concentrations (i.e., the schematic configurations in Figure 6.4 are the same for low H coverage).



Energy Landscape

Figure 6.4: Predicted potential energy diagram for NO evolution from the NO₂ and H co-adsorbed Au(111) surface. This diagram indicates the intermediate and transition state configurations on Au(111) with high pre-covered H at $\theta_{\rm H} =$ 1. Note that the configurations of surface species are not affected by H coverages. The big yellow, small blue, red, and white balls indicate Au, N, O, and H atoms, respectively.

We first investigate the initial NO₂ activation on H-covered Au(111) by calculating the adsorption energy of NO₂ and the reaction energetic/barrier for NO₂ + H \rightarrow HNO₂. As shown in Figure 6.4 and Table 6.1, we find that on the H saturated surface ($\theta_{\rm H} \sim 1$ or $\theta_{\rm E} \sim 0$), NO₂ exothermically adsorbs [$E_{\rm ad} = 0.30$ eV] at the top-bridge-top site with the two O moieties of NO₂ bonded to Au atoms on H-covered Au(111). In the next step, we see that adsorbed NO₂ can readily react with neighboring H adatoms with a very low barrier (0.04 eV), producing a *cis* form of HNO₂ (indicated by H_{dw}ONO where H points towards the surface). Here, the rotational barrier of the H atom in H_{dw}ONO for forming a *trans* HNO₂ (H_{up}ONO where H points away from the surface) is predicted to be 0.28 eV. Together with the exothermic NO₂ adsorption energy, this result suggests that NO₂ can be trapped in the form of H_{dw}ONO or H_{up}ONO on H-covered Au(111) at 77 K.

This process dominates the early period in the MBRS measurement from 0 - 5sand represents the initial induction period [the period i) – ii)] before the evolution of NO, as shown in Figure 6.1b. The computational results display the relatively high barriers for the reaction of HNO₂ with neighboring H atoms during the induction period (H + $H_{up}ONO \rightarrow NO + H_2O$, $E_a = 0.47$ eV. Note that we only focus on the $H_{up}ONO$ state because the reaction between $H_{dw}ONO$ and H always occurs via the $H_{up}ONO$ state), implying that NO cannot evolve at 77K. Our TPD results show desorption peaks for NO and H_2O at ~ 120 K and ~ 150 K, respectively, as displayed in Figures 6.3a and 6.3b. We also compared other possible reaction mechanisms for NO production such as $NO_2 \rightarrow$ NO + O ($E_a = 1.98eV$) and $H_{up}ONO \rightarrow NO + OH$ ($E_a = 0.81eV$), both of which have a higher energetic barrier and cannot be considered viable mechanisms. Due to the high barrier for HONO dissociation and the ease of NO_2 trapping by H adatoms (which is exothermic by 1.13 eV), we think that the single-step Eley-Rideal (ER) reaction of $NO_2(g) + H \rightarrow OH + NO(g)$ is highly unlikely. In addition, the induction period we observe also indicates that the reduction of NO2 to NO is not following an ER mechanism. Otherwise, NO would evolve immediately after the NO₂ beam strikes the H/Au(111) surface (at t = 0 s).



Figure 6.5: 20 s of NO₂ impingement to Au(111) pre-covered by various converges of hydrogen (a) and deuterium (b) at 77 K. The QMS was employed to monitor mass 30, 46, and 2 (or 4). Note that (a) and (b) have the same scale in the Yaxis.

With further exposure of NO₂ to the surface by the beam, NO begins to evolve from the surface. This production of NO at 77K is related to the reduction of the barrier for the reaction H + H_{up}ONO \rightarrow NO + H₂O due to the increase of available empty surface sites near H_{up}ONO (called "near empty sites" in later discussion) through H₂ desorption which has been observed during MBRS as shown in Figure 6.1b. Our previous study indicated that H atoms weakly chemsorb on Au(111) and H₂ recombinative desorption has a small activation energy of ~ 0.28 eV.^{33,54} In contrast, the adsorption of NO₂ on H/Au(111) and HNO₂ formation are exothermic processes and release heat (0.30 eV and 1.13 eV, respectively as shown in Table 6.1), which likely activate a fraction of the H adatoms leading to recombinative H₂ desorption at 77 K.

According to our DFT calculations, the barrier for H + $H_{up}ONO \rightarrow NO + H_2O$ strongly depends on the number of near empty surface sites around HNO2. A larger number of near empty surface sites leads to a lower a reaction barrier. In Table 6.1, we display the barriers for the surface reaction H + $H_{up}ONO \rightarrow NO + H_2O$ for different coverages of neighboring empty surface sites around HNO₂. We find that the barrier (E_a = 0.30 eV) at $\theta_E \sim 1$ is substantially lower than the $\theta_E \sim 0$ case ($E_a = 0.47$ eV), implying that the large availability of near empty surface sites around HNO₂ plays an important role in enhancing NO evolution through the H + H_{up} ONO reaction at 77 K. Therefore, it can be concluded that the induction period prior to NO evolution at 77 K is partly due to the time needed for generation of near empty sites. Figure 6.5a shows that lower initial H coverages cause a longer induction period and smaller production of NO during MBRS, indicating that the formation of HNO2 is a rate-determining step which is promoted by high coverage of H adatoms as shown in Table 6.1. These results suggest that NO evolution is not only affected by reaction kinetics but also influenced thermodynamically. The use of deuterium lengthens the induction period and signifycantly reduces the production of NO by a factor of 10 as shown in Figure 6.5b. These experimental results could be due to quantum tunneling of H/D and a primary kinetic isotope effect.

Additionally, a portion of the nascent NO directly evolves from the surface at 77 K whereas the other part reacts with adsorbed NO₂ on the Au(111) surface via the reaction NO +NO₂ \rightarrow N₂O₃ where dinitrogen trioxide is generated as the second intermediate (DFT calculations show a barrier of 0.27 eV for NO + NO₂ \rightarrow N₂O₃). Annealing the sample surface causes the thermal dissociation of intermediate N₂O₃ producing NO and NO₂ as shown in Figure 6.3a(*iii*). TPD measurements indicate that H adatoms are depleted at the end of NO evolution ($t = \sim 15$ s). During the period from point (*iii*) to (v) in Figure 6.1b, a large fraction of NO₂ molecules adsorb intact on the surface with low reaction probability due to the lack of H adatom coverage.



Figure 6.6: TPD spectra of H₂O and NO₂ co-adsorbed on Au(111) with varying H₂O coverages. All species were dosed on the surface at 77 K. The heating rate was 1 K/s.

DFT calculations indicate that water is produced from the reactions $H + NO_2 \rightarrow$ HNO₂ and $H + HNO_2 \rightarrow NO + H_2O$. Thus, the production of water is correlated to the

concentration of surface hydrogen atoms. In addition, Koel has reported that NO₂ has a strong interaction with water on Au(111) and can stabilize water resulting in desorption at a higher temperature.⁵⁵ Figure 6.6 indicates that water can be stabilized by NO₂ on the surface yielding a desorption peak temperature at ~ 190 K. This is in agreement with the TPD spectra for water in Figure 6.3b: 1) at t = 5 s NO₂ is fully converted to NO via an HNO₂ intermediate and thus, is unavailable to interact with the adsorbed water, so there is a single water desorption feature at ~ 150 K; 2) at t = 10 s NO₂ is produced via N₂O₃ decomposition and interacts with water, shifting the desorption feature to the higher temperature of ~ 190 K; 3) with further NO₂ impingement and the surface reaction progressing (to t = 15 and 20 s) more water is generated on the surface and induces a desorption feature again at 160 K. In addition, Figure 6.7 shows TPD experiments with fixed NO₂ coverage but varying H coverages on Au(111). Figure 6.7b shows that water has a single desorption feature at ~190 K for low H coverages and induces the other desorption feature at ~ 160 K with increasing H coverages (i.e., more water is formed). This series of experiments clearly indicates that water desorption is NO₂ concentration dependent on co-adsorbed H/Au(111), consistent with the above discussion.

To enhance microscopic understanding of NO₂ reduction, vibrational spectroscopy was employed to study the Au(111) surface co-adsorbed with H adatoms and NO₂ at 77 K. Figure 6.8a shows vibrational spectra for NO₂ on clean Au(111) with varying coverages as a control experiment and the infrared (IR) spectra are in excellent agreement with previously published results by Wang and Koel^{55,56}. The distinct absorption peaks for fundamental vibrational modes of NO₂ are evident at 1182 and 808 cm⁻¹ which correspond to $v(NO_2)$ (symmetric and asymmetric stretching vibrations) and $\delta_s(NO_2)$ (symmetric bending mode) normal modes, respectively. At $\theta = 1.0$ ML, the dimer of NO₂ is formed with the features for N₂O₄ at 1759, 1298, and 784 cm⁻¹ which are

attributed to the $v_a(NO_2)$, $v_s(NO_2)$ and $\delta_s(NO_2)$ modes, respectively. In addition, peaks are apparent at 1907 and 1256 cm⁻¹ indicating features for N₂O₃ with the v(NO) and $v_a(NO_2)$ modes, which are reported by Wang and Koel from the reaction between background NO and surface NO₂.⁵⁶



Figure 6.7: TPD spectra of mass 30, 46, 18 after 20s of NO₂ impingement on Au(111) pre-covered by various coverages of hydrogen at 77 K. Note that (a) and (b) have the same scale for the *Y*-axis.



Figure 6.8: RAIRS spectra of NO₂. RAIRS measurements were conducted on (a) clean Au(111) and (b) $\theta_{H,rel} = 1$ of H-pre-covered Au(111). In MRBS experiments, NO₂ was impinged onto H/Au(111) at 77 K reaching the end of the induction period (the beginning of NO evolution) at point *(ii)*, the peak of NO evolution at point *(iii)*, and the end of NO evolution at point *(iv)* as illustrated in Figure 6.1b. Note that (a) and (b) have the same scale for the *Y*-axis.

After adsorbing NO₂ on the H pre-covered surface and achieving a variety of reaction stages [(*ii*), (*iii*) and (*iv*)], we acquired RAIRS spectra at 77 K revealing significant differences in comparison to the control experiments on the clean surface. Figure 6.8b shows most of the characteristic features for NO₂, N₂O₄ and N₂O₃ on

H/Au(111), however the intensities are noticeably diminished compared to Figure 6.8a indicating a decrease in the NO₂ concentration due to the reaction with H adatoms. However, with H co-adsorbed on the surface, we observe a new feature located in the range of 1850 - 2000 cm⁻¹, which could result from reaction intermediates, HNO₂ and N_2O_3 . We propose this band be assigned to the v(NO) mode in HNO₂ or in N_2O_3 respectively. The transformation from HNO₂ to N₂O₃ with NO₂ coverage increasing on the surface blue-shifts the new feature from 1889 to 1918 cm⁻¹. Additionally, we examined the IR spectra after heating the surface to various temperatures regarding those three stages as shown in Figure 6.9. The feature at 1889 cm⁻¹ decreases upon heating the surface to 125 K. In contrast, the 1918 cm⁻¹ feature is more stable and remains constant until annealing the sample to 150 K. This observation confirms that those two features are responsible for the different surface species - HNO₂ and N₂O₃. We also note that a feature at 1182 cm⁻¹ appears when heating the surface to above 150 K, indicating the formation of NO₂ which likely stems from the decomposition of N₂O₃. The surface infrared spectroscopy measurements at various reaction stages show consistency with MBRS, TPD and DFT results, clarifying the formation of two intermediates (HNO₂ and N_2O_3).



Figure 6.9: RAIRS spectra of (a) 0.5 ML, (b) 1.0 ML, and (c) 1.5 ML NO₂ adsorbed on $\theta_{H,rel} = 1$ of H-pre-covered on Au(111). NO₂ was impinged onto H/Au(111) at 77 K via molecular beam following by incremental heating to each temperature. The sample is cooled to 77 K before collecting each spectrum. Note that (a), (b) and (c) have the same scale for the *Y*-axis.

CONCLUSIONS

In summary, we have observed NO₂ reduction to NO on the H atom pre-covered Au(111) surface at 77 K. During MBRS measurements, adsorbing NO₂ on H/Au(111) causes NO to evolve from the surface at 77 K after a brief induction period. The reaction during the induction period yields a high NO₂ conversion (100 %) and remarkable selectivity (100 %) towards NO (for low NO₂ coverages with annealing to 120 K) revealing unique catalytic properties for gold in hydrogenation reactions. TPD investigations also provide detailed information demonstrating the production of NO and water upon heating the surface. A mechanism is proposed concerning HNO₂ and N₂O₃ as intermediates which are identified by infrared spectroscopy and DFT calculations. Further, this study shows that weakly bound hydrogen plays a key role in hydrogenation chemistry on gold surfaces and provides some fundamental understanding of the high activity of gold-based catalysts for selective hydrogenation processes.

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Chapter 7: Concluding Remarks and Future Research

OVERVIEW OF COMPLETED WORK

Gold-based catalysts have been studied for many hydrogenation reactions, showing remarkable activity, particularly for selective transformations. However, the related fundamental studies on model gold surfaces are lacking and highly desired in order to provide reaction mechanisms. This dissertation demonstrates studies on hydrogenation reactions on a Au(111) single crystal surface using atomic hydrogen to pre-populate the surface. These studies aim to understand the role of gold in hydrogenation reactions after dissociated H atoms diffuse onto the gold surface, and further provide insight into the catalytic properties of classical supported gold nanoparticle catalysts. Our model studies show the following interesting experimental results:

(i) Hydrogen adatoms weakly bind on Au(111) with a desorption peak at 110K, indicating an activation energy for recombinative desorption of ~28 kJ/mol.

(ii) Acetaldehyde can be hydrogenated to ethanol on H-pre-covered Au(111). The Au(111) surface shows activity for propionaldehyde hydrogenation to 1propanol but not for acetone hydrogenation to 2-propanol. This difference is due to dissimilarities in the energetic barriers of the reaction steps and that polymerization of propionaldehyde allows the molecules to remain on the surface at higher temperatures, increasing the reaction probability.

(iii) Ethers can be synthesized via a coupling reaction of aldehydes or aldehyde-alcohol on H/Au(111), where the alcohol-like intermediate from the partial hydrogenation of aldehydes plays a key role for the production of ethers.

(iv) Water has a strong interaction with H on Au(111) and shows H/D exchange in isotopic experiments, indicating dissociation of the O-H group. The
isotopic experiments also help to identify the sources of desorption features of H_2 (from surface H atoms or H in water), allowing speculation regarding a reaction mechanism.

(v) The reduction of nitrogen dioxide occurs at cryogenic temperatures on H/Au(111), yielding a high NO₂ conversion (100 %) and NO selectivity (100 %) upon heating the sample to ~ 120 K. HNO₂ and N₂O₃ are the reaction intermediates.

In summary, the model gold surface, Au(111), shows a unique catalytic activity for selective hydrogenation reactions. Weakly bound H atoms demonstrate reactivity for hydrogenation reactions and can yield a high selectivity for partially hydrogenated products. The aim of this work was to provide additional mechanistic information for gold catalytic activity for hydrogenation reactions and enhance the understanding of hydrogenation chemistry of classical supported gold catalysts at the molecular scale.

PRACTICAL IMPACTS

In this work, atomic hydrogen has been directly used to populate the Au(111) surface for studying hydrogenation reactions. This method is able to create a model system to simulate the atomic hydrogen migration onto the gold face sites after molecular hydrogen dissociates on other active sites, and fundamentally investigate the role of gold in hydrogenation transformations on a classical catalytic system. However, whether H atoms can spillover/diffuse onto other portions of the gold surface after dissociating on active sites, such as low-coordinated gold sites and interfaces, is still an open question.

Generally, H_2 dissociation has been considered as a key step for hydrogenation reactions. Norskov and coworkers conducted density functional theory (DFT) calculations and predicted that H_2 dissociation has a high energetic barrier and is

activated on a Au(111) surface.¹ However, for classical gold catalysts, H₂ dissociation likely occurs at low-coordinated sites and/or the interface between the gold particles and the metal oxide support. Fujitani and coworkers observed H-D production from H₂ and D_2 by using two types of model catalysts - Au/TiO₂(110)² and TiO₂/Au(111),³ and they provided evidence that H₂ dissociation occurs at the interface of the gold particles and TiO₂. However, Yates and Morris employed transmission Fourier transform infrared (FTIR) spectroscopy and CO oxidation as a probe reaction to demonstrate that the most active sites for hydrogen dissociation on Au/TiO₂ are the free step edges or other defect sites on Au particles.⁴ Additionally, they found that dissociated atomic H can diffuse to the TiO₂ support, possibly via spillover onto the flat Au faces.⁴ Therefore, we speculate that after H₂ dissociation on defect or interface sites, the subsequent hydrogen atoms will "spill over" onto the predominantly Au(111) face of the gold particle, and these activated hydrogen atoms are the reactive species for some hydrogenation reactions occurring on gold catalysts. Thus, in order to conduct fundamental studies regarding hydrogenation on a model gold surface such as Au(111), it is necessary to populate the surface with atomic hydrogen to simulate H₂ dissociation and spillover onto the surface.

In addition to the Yates and Morris research,⁴ Bron and coworkers studied hydrogenation of acrolein on Ag high-surface-area catalysts and suggested that H_2 dissociates on defect sites on silver particles and spills over onto the face sites.⁵ Since H atoms have similar binding energies on Ag(111) and Au(111) based on DFT calculations⁶ and TPD (temperature programmed desorption) measurements,^{7,8} it is reasonable to speculate that H atoms might also be able to diffuse onto gold face sites after H_2 dissociation at a defect or interface site. If hydrogen atoms are able to spill over onto the flat Au surface, these hydrogen atoms likely contribute significantly to the reactivity for hydrogenation reactions on gold.

Sykes and coworkers addressed this issue by employing scanning tunneling microscopy (STM) to study H₂ adsorption on Pd/Au(111).^{9,10} They exposed the sample to H₂ at 420 K and then cooled it to 7 K, after which they did not detect any H atoms on the Au surface via STM. They suggested that H atoms cannot diffuse onto the Au(111) surface from the Pd-Au interfaces due to the strong binding energy at the interface. However, since they exposed the Au(111) sample to H_2 at 420 K,¹⁰ it cannot be ruled out that the generated H atoms did diffuse on to the Au(111) surface, but then immediately recombined to desorb from the surface at this elevated temperature. Similarly, Bus and coworkers studied H₂ dissociation on Al₂O₃-supported gold catalysts and also suggested that the generated H atoms cannot diffuse onto gold face sites.¹¹ Using EXAFS (extended X-ray adsorption fine structure) techniques to estimate Au particle size and number of surface Au atoms, they estimated the ratio of H/surface Au atoms during hydrogen chemisorption to be lower than 100 %, and increases with reducing gold particle size, suggesting H atoms do not bind to all the exposed sites on gold particles and likely adsorb only on the low coordinated sites that they dissociated on, such as edges and corners.¹¹ However, the catalysts were tested at 298 K or higher temperatures, which again likely causes immediate H₂ recombinative desorption after diffusing onto the face sites. While the authors of both of these studies suggest that hydrogen atoms do not spillover, neither of above two studies can definitively disprove the ability for hydrogen atoms to "spill over" onto gold surfaces.

Since active hydrogenation chemistry has been observed classically on supported gold catalysts, we conducted the studies reported in this dissertation regarding hydrogenation reactions on a Au(111) model surface in order to better understand the role of gold in hydrogenation transformations on classical Au-based catalysts and to provide insights into the reaction mechanisms.

ONGOING AND FUTURE RESEARCH

Hydrogenation Reactions on Au(111)

	Desorption
Reactant on H/Au(111)	temperature on clean
	Au(111)
СО	90 K
CO_2	90 K
C_2H_4	90 K
NO	90 K
N_2O	90 K
CH ₂ =CH-CHO	160 K*, **
C ₆ H ₅ CHO	260 K**
CH ₃ CH ₂ CH ₂ CH ₂ C≡CH	210 K**

* The reaction can be detected but the reactivity is very small. ** The temperature is the peak of monolayer desorption.

Table 7.1:Experiments on the hydrogen covered Au(111) surface not showing
hydrogenative reactivity.

In this work, while we have successfully demonstrated several hydrogenation reactions that occur on Au(111) as discussed in this dissertation, we have also been unsuccessful in some of our attempts to catalyze a hydrogenation reaction on the Au(111) surface. Table 7.1 lists experiments that we examined on the Au(111) surface but for which no reactivity has been detected.

No measurable activity can be the result of a few different scenarios. First of all, it is possible that gold cannot catalyze the hydrogenation reaction at all, which can be further studied with classical gold catalyst experiments or more extensive model catalyst experiments. Secondly, the hydrogen atoms and/or the other reactant(s) are weakly bound to the surface, and desorb off the surface at temperatures lower than that required to drive the chemical reaction. While this is a limitation in the model experiments, it does not disprove the ability for gold to catalyze a particular reaction. At ambient temperatures and pressures associated with classical gold catalysts, the large number of collisions can result in temporarily adsorbed species with enough energy to drive the reaction. Finally, the reaction may not occur on the Au(111) surface alone, and may require a low-coordination site, such as a step or edge, or an interface between the gold and the metal oxide. Despite these previous unsuccessful experiments that we conducted, there are still some reactions which could possibly occur on the Au(111) surface in vacuum and can be included in our future work.

Hydrogenation of Benzene and its Derivatives

We plan to study benzene hydrogenation on Au(111) since it is an important process in chemical industry, where the products could be cyclohexane and cyclohexene.¹²⁻¹⁴ However, to our best knowledge, no one has carried out a fundamental study on Au(111) with H atom adsorption. We have already studied benzaldehyde on H/Au(111) and not detected hydrogenated products. For the future work, we propose to conduct more studies, such as the hydrogenation of amine groups on benzene derivatives. The project is inspired by Hatura's recent paper regarding the so-called "one-pot" synthesis of symmetric secondary amine from primary amine on supported gold clusters.¹⁵ In this process, they used oxygen to convert benzylamine (C₆H₅CH₂NH₂) to *N*- benzylidenebenzylamine which was subsequently hydrogenated to dibenzylamine with addition of H₂. A remarkably high yield (91 %) of dibenzylamine was obtained.¹⁵ We plan to investigate the hydrogenation of N-benzylidenebenzylamine on Au(111) preadsorbed by H and D atoms, in which employing deuterium could help us to identify the products.

Hydrogenation of Furan

A fundamental surface science study of the adsorption and reactions of fivemembered aromatic molecules is important to the petrochemical industry including the hydrodenitrogenation, hydrodesulfurization, and hydrodeoxygenation processes.¹⁶ Recently, Somorjai and co-workers studied the hydrogenation of furan on Pt(111) and Pt(100) at Torr pressures (1 Torr of furan, 100 Torr of H₂), showing the formation of dihydrofuran, tetrahydrofuran, and the ring-cracking products butanol and propylene.¹⁶ However, the adsorption and hydrogenation of furan have received much less attention on gold-based catalysts. We will investigate the same reaction on H atom pre-covered Au(111) under UHV conditions. If furan shows reactivity for hydrogenation on Au(111), we will carry out a detailed study including the examination of reactant coverage for optimum productivity and the investigation of a possible kinetic isotope effect using deuterium atoms. We may also employ FTIR vibrational spectroscopy and DFT calculations to interpret the related mechanism. Interaction of Aldehydes and Alcohols on H/Au(111)



Figure 7.1: TPD spectra of acetaldehyde and 1-propanol from (a) 0.70 ML $CH_3CH_2CH_2OH$ on Au(111) with co-adsorption of 0.65 ML CH_3CHO and $H (\theta_{H,rel} = 0.74)$, (b) 0.70 ML $CH_3CH_2CH_2OH$ on Au(111) with preadsorption of 0.65 ML CH_3CHO , and (c) 0.65 ML CH_3CHO on Au(111) with co-adsorption of 0.70 ML $CH_3CH_2CH_2OH$ and $H (\theta_{H,rel} = 0.74)$. All species were adsorbed on the surface at 77 K. The heating rate was 1 K/s. Note that (a), (b) and (c) have the same scale on the y-axis.

In Chapter 4, we discussed the research regarding ether production via coupling of aldehydes and alcohols on H covered Au(111). During the experiments, we observed an interesting phenomenon for aldehyde desorption. Figure 7.1 shows an example where 1-propanol and acetaldehyde were co-adsorbed on H/Au(111). The TPD results indicate that acetaldehyde very rapidly desorbs from the surface in a small temperature range (2

K) showing a sharp desorption feature at ~ 190 K as illustrated in Figure 7.1a. Plots (b) and (c) result from the control experiments and indicate that adsorbing both H atoms and acetaldehyde before 1-propanol is indispensable for causing this phenomenon. Based on our work, acetaldehyde can polymerize on a H covered Au(111) surface as discussed in Chapter 2. This polymer is likely not stable and could readily decompose upon heating, leading to a sharp desorption feature of acetaldehyde. However, more work is needed to better understand this experimental result. Some surface techniques such as vibrational spectroscopy and theoretical calculations could be useful for this study.

Other Catalytic Systems – Complex Model Catalysts and Classical Catalysts

In addition, our group can operate physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques to prepare multi-component model catalytic systems, which could assist us in investigations of reactions on comparably complicated catalysts to collect mechanistic information. Our group has already studied CO oxidation on multi-component gold based model catalysts, such as $Au/TiO_2(110)^{17}$ and $Fe_2O_3/Au(111)$.¹⁸ This research aims to assess related mechanistic information for supported catalysts which have potential application to fuel cell processing and clean energy development. Using the related knowledge and experience, we can prepare those multi-component model catalysts to study hydrogenation reactions which have already been investigated on the model gold (111) surface, as discussed in this dissertation. These studies can enhance the understanding of gold surface chemistry in hydrogenation and further enable the transformation between our research results to the studies on classical gold catalysts.

Currently, we are building a new experimental apparatus, a Plug Flow Reactor (PFR) that uses a Gas Chromatography (GC) system for analysis. We hope to learn more about classical, high surface area catalysts and study hydrogenation reactions over

practical gold-based catalysts. This effort will allow us to bridge the knowledge between classical and model catalytic systems. Such parallel studies will supply a powerful tool for identifying the individual mechanistic effects of metallic particles, metal oxide support, and their interface, which has been a constant challenge in the study of catalysts. In addition, when a novel surface chemical reaction is observed on model gold catalysts, the classical catalytic system can be used to conduct more kinetic and thermodynamic studies to explore the potential for an industrial manufacturing application. This synergetic research enhances the understanding of classical catalytic systems from a mechanistic point of view and provides the basis for predictive catalyst design, enabling faster development of more effective catalysts. Based on the experimental results from the model gold system, we have planned to start an investigation of NO₂ reduction and ether synthesis on classical gold catalysts, both of which demonstrate interesting catalytic properties of gold surfaces and have important industrial applications.

In addition, we will also maintain our collaboration with theoretical research groups and use their modeling knowledge to interpret our experimental results. Therefore, the ultimate goal of our research is use certain chemical reactions to broadly study catalysts from fundamental understanding to practical applications. This can be supported by the miscellaneous capabilities of our group, including DFT calculations (with collaboration), model catalysts, and a classical catalytic system.

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Appendix A: Atomic Oxygen Induced CO Dissociation on Ir(111) INTRODUCTION

CO dissociation on transition metals is a key step for Fischer-Tropsch synthesis (FTS) and needs to be fundamentally understood.¹ The FTS process, which produces hydrocarbons from CO and hydrogen, has received widespread attention as an alternative to petroleum.² Thus, adsorption and dissociation of CO have been investigated experimentally and theoretically on group-VIII transition metals (Fe,³ Pt,⁴ Ni,⁵ Co,⁶ Rh,⁷ Ru,⁸ and Pd⁹) and non-VIII group transition metals (Mo,¹⁰ W,¹¹ Ag,¹² and Cu¹³). The reactivity of transition metals for CO dissociation has generally been found to decrease when starting from the upper left moving down to the right in the periodic table.^{14,15}

Using low energy electron diffraction and temperature programmed desorption (TPD), Ertl *et al.* reported that CO dissociated on Ir(110) at ~473 K. In addition to the characteristic desorption feature for CO at ~ 448 K, two new peaks at ~ 513 and ~ 633 K were assigned to recombination of dissociated CO.¹⁶ Since the (111) facet is more stable and readily formed in classical catalysts, Weinberg *et al.* later studied CO on Ir(111) employing UV- and X-ray photoelectron spectroscopy and found that CO adsorbed intact on Ir(111) even at temperatures up to 533 K.¹⁷ Mavrikakis *et al.* have studied CO dissociation using density functional theory calculations and found evidence for an exothermic CO dissociates at low temperatures (less than 400 K) in the presence of either oxygen or water (or both) adsorbed on an Ir(111) surface. It has been found that adsorbed alkali metals^{8,19,20} or hydrogen atoms²¹ can assist in CO dissociation, however, to the best of our knowledge this is the first time adsorbed oxygen atoms or hydroxyl groups (due to water dissociation/interaction of oxygen)

with water) have been observed to induce CO dissociation on metal surfaces.

EXPERIMENTAL SECTION

All experiments were conducted in a supersonic molecular beam surface scattering apparatus in which the ultrahigh vacuum scattering chamber has a base pressure less than 2×10^{-10} Torr. The scattering chamber is equipped with an Auger electron spectrometer (AES), low energy electron diffraction optics (LEED), and a quadrupole mass spectrometer (QMS). A detailed description has been previously reported²² and also been included in Chapter 2.

A circular Ir(111) sample with a diameter of ~1 cm was employed, which can be resistively heated to 1550 K and rapidly cooled to 77 K by liquid nitrogen. Research purity ${}^{16}O_2$, $H_2{}^{16}O$, and isotopically labeled reagents (i.e., $H_2{}^{18}O$ and ${}^{13}C{}^{18}O$) were employed in this study. A molecular beam of each of the reagents (other than ${}^{13}C{}^{18}O$) was introduced into the scattering chamber using a device consisting of separated nozzles, each with the same aperture size and separate plumbing to insure reagent purity as delivered to the sample. ${}^{13}C{}^{18}O$ was backfilled into the scattering chamber and adsorbed on Ir(111). The coverage of each gas (CO and O₂) was estimated based on LEED measurements for saturated coverages that are in agreement with those reported previously.^{23,24} Water was dosed on the sample at a rate of 0.067 monolayer (ML)/s. Referring to the water structure on Pt(111), the density of 1 ML water was estimated to be 1.23×10^{15} molecules/cm².²⁵ The sample was cleaned by Ar ion sputtering followed by annealing in gaseous oxygen.

In this study, we can observe two indicators of CO dissociation on oxygen and/or water co-adsorbed Ir(111) surface, which are products from partial and full oxidation of carbon from CO dissociation. In general, we found that the main indicator is the product

of partial carbon oxidation, which has a higher yield. Based on the TPD integrated areas of these two indicators, we can calculate the CO dissociation probability.

If we used ${}^{13}C^{18}O$ in experiments as shown in Figure A.2 and 3, the indicators are ${}^{13}C^{16}O$ and ${}^{13}C^{16}O^{16}O$. We compared the TPD integrals of ${}^{13}C^{18}O$, ${}^{13}C^{16}O$ and ${}^{13}C^{16}O^{16}O$ on the clean surface (represented by A) and the O/OH modified surface (represented by B). Thus, the equation of CO dissociation probability is shown as follows:

CO Diss. Prob.
$$\% = \frac{(B_{13}C^{16}O} - A_{13}C^{16}O}{A_{13}C^{16}O} + (B_{13}C^{16}O^{16}O} - A_{13}C^{16}O^{16}O}) \times 100\%$$

Similarly, the indicators of CO dissociation are ${}^{12}C^{18}O$ and ${}^{12}C^{18}O^{18}O$ when we employed $H_2{}^{18}O$ (see Figure A.4). Also, we used A and B to represent the integrated areas of TPD spectra of species desorbed from clean and OH modified surfaces, respectively. The equation is shown here:

CO Diss. Prob.
$$\% = \frac{(B_{12}C^{18}O - A_{12}C^{18}O) + (B_{12}C^{18}O^{18}O - A_{12}C^{18}O^{18}O)}{A_{12}C^{16}O^{-12}C^{16}O_{background}} \times 100\%$$

where background ${}^{12}C^{16}O$ was monitored by ramping the "clean" Ir(111) surface to 1550 K.

RESULTS AND DISCUSSION

We begin our description of CO dissociation by examining the interaction of CO with clean Ir(111). we co-adsorbed 0.12 ML ${}^{12}C{}^{16}O$ and 0.14 ML ${}^{13}C{}^{18}O$ on the Ir(111) surface between 89 and 77 K and searched for the production of scrambled recombination products, ${}^{13}C{}^{16}O$ and ${}^{12}C{}^{18}O$ (${}^{12}C{}^{16}O{+}{}^{13}C{}^{18}O{-}{}^{13}C{}^{16}O{+}{}^{12}C{}^{18}O$), in temperature programmed desorption (TPD) spectra. First, two blank experiments were conducted with adsorption (separately) of either (i) ${}^{12}C{}^{16}O$ or (ii) ${}^{13}C{}^{18}O$. Figure A.1

displays the integrated areas of TPD spectra with the red column denoting desorption of 0.14 ML ${}^{13}C^{18}O$, the blue column representing desorption of 0.12 ML ${}^{12}C^{16}O$, and the green column denoting desorption of the co-adsorbed carbon monoxides $(0.12ML {}^{12}C^{16}O)$ and 0.14 ML ¹³C¹⁸O). Note that the amount of desorbed ¹³C¹⁶O [an indicator of dissociation] from the co-adsorbed ${}^{13}C^{18}O$ and ${}^{12}C^{16}O$ on the Ir(111) surface is very similar to the sum of the mass 29 in the two blank experiments (i.e., the green column is very nearly equal to the sum of the red and the blue columns in the columns labeled $^{13}C^{16}O$ in Figure A.1). Furthermore, similar phenomena were observed regarding desorbed ¹²C¹⁸O [also an indicator of CO dissociation in these experiments], indicating that the detected scrambled products (${}^{13}C^{16}O$ and ${}^{12}C^{18}O$) are actually simply due to the impurities in reactant CO rather than due to CO dissociation. Additionally, the quantity of reactant gases ¹²C¹⁶O and ¹³C¹⁸O detected in the co-adsorption experiment [represented by the green column] is approximately equal to the sum of that in the blank experiments, further suggesting no mixing or dissociation. Therefore, we conclude that CO dissociation on clean Ir(111) is small and immeasurable by our techniques. We estimate that the smallest value of the CO dissociation probability that we would be able to measure is ~ 0.2 %.

Although CO oxidation has been previously investigated on oxygen covered Ir(111),^{26,27} the influence of oxygen on CO dissociation has not been reported. Here, we examine the effect of adsorbed oxygen employing isotopically labeled ¹³C¹⁸O. Figure A.2 shows the desorption of ¹³C¹⁶O (an indicator of dissociation) from Ir(111) with two different coverages of ¹⁶O_a [O₂ dissociates on clean Ir(111)^{28,29}] after pre-adsorbing 0.25 monolayer (ML) of ¹³C¹⁸O. Firstly, a measurable amount of ¹³C¹⁶O was detected desorbing from oxygen free Ir(111) [black curve] due to impurities in the ¹³C¹⁸O (~ 3%). However, the amount of ¹³C¹⁶O produced increases as a function of increasing ¹⁶O_a

coverage, indicating the promotional effect of oxygen adatoms on CO bond cleavage. The dissociation probability of CO increases from ~ 4 to ~ 7 % with increasing O_a coverage [from 0.06 (red curve) to 0.15 ML (blue curve)] and increases further with higher oxygen coverages [the method for estimating CO dissociation probability is described in the supplementary information, where both dissociation indicators ($^{13}C^{16}O$ and $^{13}C^{16}O^{16}O - ^{13}C^{16}O$ is main indicator and has higher yield) were considered]. We speculate that oxygen atoms enhance CO dissociation through weakening of the C-O bond and strengthening of the surface-CO interaction.



Figure A.1: Integrated desorption of ¹²C¹⁶O, ¹³C¹⁸O, ¹²C¹⁸O, and ¹³C¹⁶O from Ir(111) covered by 0.12 ML ¹²C¹⁶O (blue column), 0.14 ML ¹³C¹⁸O (red column) and co-adsorbed 0.12 ML ¹²C¹⁶O/0.14 ML ¹³C¹⁸O (green column). All species were dosed onto the surface between 89 and 77 K. The heating rate during TPD was 10 K/s.



Figure A.2: TPD spectra of ${}^{13}C^{16}O$ (m/e = 29) from various ${}^{16}O_a$ coverages (0, 0.06, and 0.15 ML) on Ir(111) pre-covered with 0.25 ML ${}^{13}C^{18}O$. All species were dosed on the surface between 89 and 77 K. The heating rate was 10 K/s.

It has been reported that water enhances CO oxidation on atomic oxygen precovered metals in UHV conditions, in which hydroxyl groups (formed via water interaction with oxygen atoms) react with CO to produce CO_2 .³⁰⁻³² Thus, we were also interested in whether adsorbed water (or co-adsorbed with oxygen) could influence CO dissociation on Ir(111). Firstly, in order to investigate the exclusive effect of adsorbed water on CO dissociation, 0.08 ML ¹³C¹⁸O and 0.28 ML H₂¹⁶O were coadsorbed on the Ir(111) surface followed by TPD monitoring ¹³C¹⁶O (*m/e* = 29), as shown by the pink curve in Figure A.3. Note that a ~ 14 % larger amount of ¹³C¹⁶O was desorbed compared to that on Ir(111) with only 0.08 ML ¹³C¹⁸O as shown by the black curve in Figure A.3 (see inset for TPD integrals). This observation can be attributed to the effect of hydroxyl groups which are produced by water dissociation on Ir(111) and apparently play a role similar to atomic oxygen. A low CO dissociation probability (~ 0.6 %) was obtained since only ~ 2 % of the water has been found to dissociate on Ir(111) [~ 6 % water dissociation on Ir(110)³³ with more active sites]. With co-adsorbed ¹³C¹⁸O (0.08 ML), H₂¹⁶O (various coverages) and ¹⁶O_a (0.15 ML) on Ir(111), we again observe CO dissociation as indicated by the production of ¹³C¹⁶O. The red curve in Figure A.3 shows the ¹³C¹⁶O (*m/e* = 29) TPD for adsorbed ¹³C¹⁸O and ¹⁶O_a only, while the blue and green curves show TPD spectra with additional water demonstrating the enhancing effect of increasing coverages of adsorbed water. Additionally, we found that the dissociation probability of CO increases from ~ 8 to ~ 10 % with increasing water coverages from 0.1 to 0.28 ML. Also note that a similar amount of ¹³C¹⁶O (was evolved on the 0.08 ML ¹³C¹⁸O and 0.15 ML ¹⁶O_a co-adsorbed Ir(111) surface (red curve), compared to the surface exclusively covered by 0.08 ML ¹³C¹⁸O (black curve), making it appear that no CO dissociation is obtained (~ 3 %) since a notable amount of ¹³C¹⁶O dissociation] was detected.

The effect of CO coverage can be seen by comparing Figure A.2 and A.3. With the same oxygen coverage (0.15ML), a four times higher ratio of ${}^{13}C^{18}O^{16}O/{}^{13}C^{16}O$ (${}^{13}C^{18}O^{16}O$ is from ${}^{13}C^{18}O$ oxidation) has been observed on 0.08 ML ${}^{13}C^{18}O$ pre-coverd Ir(111) (the red curve in Figure A.3) than that on 0.25 ML ${}^{13}C^{18}O$ covered Ir(111) (the blue curve in Figure A.2) and the CO dissociation probability is reduced by ~ 2, suggesting that low CO coverage (or high O coverage) probably favors CO oxidation and suppresses CO dissociation on Ir(111).

Enhancement of CO dissociation by co-adsorbed water and oxygen suggests an interaction between oxygen and water. TPD of co-adsorbed $H_2^{18}O$ and ${}^{16}O_a$ on Ir(111), produces new features for mass 18 ($H_2^{16}O$) and 20 ($H_2^{18}O$) at 235 K in 137 addition to the characteristic desorption peaks for water at 157 K (multilayer) and 175 K (monolayer). Adsorbed hydroxyl groups (OH_{ad}) are considered to be the intermediate in this process ($O_a + H_2O_a = 2OH_a$) and to induce dissociation. Water dissociation on oxygen covered metals has been reported on a variety of other transition metal surfaces.^{30,31,34-39}



Figure A.3: The pink curve is TPD spectra of ${}^{13}C^{16}O$ from co-adsorption of 0.08 ML ${}^{13}C^{18}O$ and 0.28 ML ${}^{12}O^{16}O$ on Ir(111). The black curve is TPD spectra of ${}^{13}C^{16}O$ from 0.08 ML ${}^{13}C^{18}O$ covered Ir(111). The other three curves display TPD spectra of ${}^{13}C^{16}O$ from ${}^{12}C^{16}O$ from ${}^{12}C^{16}O$ from ${}^{12}O^{16}O$ (0.28 ML in green curve, 0.1 ML in blue curve, and 0 ML in red curve) and 0.15 ML ${}^{16}O_a$ co-adsorption on 0.08 ML ${}^{13}C^{18}O$ pre-covered Ir(111). Inset graph shows the integrated areas of each TPD spectrum with the responding color filled. All species were dosed on the surface between 89 and 77 K. The heating rate during TPD was 10 K/s.

In order to further confirm and explore effects of co-adsorbed water and oxygen on CO dissociation, additional experiments were performed by using a different isotopically labeled reactant (i.e., $H_2^{18}O$) together with ${}^{12}C^{16}O$ and ${}^{16}O_a$, and examining production of the dissociation indicator ${}^{12}C^{18}O$ (*m/e* = 30). Figure A.4 displays TPD spectra of ${}^{12}C^{18}O$ (*m/e* = 30) from Ir(111), in which the blue curve shows results from sequential adsorption of 0.12 ML ${}^{12}C^{16}O$, 0.29 ML of $H_2{}^{18}O$, and 0.16 ML ${}^{16}O_a$ further indicating that adsorbed water interacts with oxygen to enhance CO dissociation [dissociation probability of CO is $\sim 10\%$ where the estimation has been determined using both indicators ¹²C¹⁸O (primary) and ¹²C¹⁸O₂]. Three control experiments were also performed to test for false indicators of dissociation. First, we investigated the effect of trace adsorbed carbon [even on extremely clean Ir(111), there is likely a minute amount of surface carbon] and/or background ${}^{12}C^{16}O$ with the $H_2{}^{18}O$ and ${}^{16}O_a$ co-adsorbed Ir(111) surface. It is well known that surface carbon readily reacts with oxygen on Ir(111) to produce CO or CO₂ (oxygen is used for cleaning).^{22,28,40-43} As the red curve clearly shows in Figure A.4, a small amount of ${}^{12}C^{18}O$ (~ 18 % of that shown in the blue curve) was observed, suggesting that neither adsorbed carbon nor background ${}^{12}C^{16}O$ can be responsible for the majority of the ${}^{12}C^{18}O$ produced. In the second control experiment (black curve), the Ir(111) surface is covered exclusively with 0.12 ML ${}^{12}C^{16}O$ and we note that the desorption of ${}^{12}C^{18}O$ was negligible (~ 0.2 % impurity in ${}^{12}C^{16}O$, comparable to the natural abundance of ¹⁸O). The third control experiment (see the green curve in Figure A.4) is similar to that shown in the blue curve except $H_2^{16}O$ was employed rather than $H_2^{18}O$, further confirming that the mass 30 signal is from ${}^{12}C^{18}O$ [rather than other species, e.g., oxygenates (-CH_xO), etc.]. The results from the control experiments demonstrate that the mass 30 (blue curve) is due to the desorption of ${}^{12}C^{18}O$ coming about from combination of ${}^{12}C_a$ (produced by ${}^{12}C^{16}O$ dissociation) and ${}^{18}O_a$ [from adsorbed isotopically labeled water ($H_2^{18}O$) on Ir(111) with atomic oxygen (${}^{16}O_a$) leading to either ${}^{18}O_a$ or ${}^{18}OH_a$].

Since CO dissociation is not common under vacuum we examined alternative pathways for CO isotopic scrambling. For example, ${}^{12}C^{16}O$ can be oxidized to ${}^{12}C^{16}O^{18}O$

(by co-adsorbed $H_2^{18}O$ and ${}^{16}O_a$) which could subsequently dissociate to ${}^{12}C^{18}O$ and ${}^{16}O_a$. Thus, we co-adsorbed ${}^{16}O_a$, $H_2^{18}O$, and ${}^{12}C^{16}O_2$ on Ir(111) and looked for formation of ${}^{12}C^{16}O^{18}O$ but none was observed. Similarly, TPD of co-adsorbed ${}^{12}C^{16}O_2$ and ${}^{18}O_a$ does not produce ${}^{12}C^{16}O^{18}O$. Both findings strongly indicate that the scrambled CO observed in previous experiments is due to CO dissociation in either the CO-O_a, CO-H₂O, or CO-H₂O-O_a systems.



Figure A.4: TPD spectra of ${}^{12}C^{18}O$ after (blue curve) 0.29 ML $H_2{}^{18}O$ and 0.16 ML ${}^{16}O_a$ adsorbed on 0.12 ML ${}^{12}C^{16}O$ pre-covered Ir(111); (red curve) 0.16 ML ${}^{16}O_a$ adsorbed on 0.29 ML $H_2{}^{18}O$ pre-covered Ir(111); (black curve) 0.12 ML ${}^{12}C^{16}O$ adsorbed Ir(111); and (green curve) 0.29 ML $H_2{}^{16}O$ and 0.16 ML ${}^{16}O_a$ adsorbed on 0.12 ML ${}^{12}C^{16}O$ pre-covered Ir(111). All species were dosed on the surface between 89 and 77 K. The heating rate during TPD was 10 K/s.

CONCLUSIONS

In this chapter, we have demonstrated that oxygen can promote CO dissociation on the Ir(111) surface, while CO dissociation on the clean surface is immeasurable. Additionally, water alone or co-adsorbed with oxygen can also induce CO dissociation on Ir(111), on which we speculate that hydroxyl groups are formed via the interaction between atomic oxygen and water and further lead to the dissociation of CO on the surface.

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Appendix B: Interaction of Water with Oxygen on Ir(111)

INTRODUCTION

Water is widely involved in catalytic processes such as the water gas shift (WGS) reaction,^{1,2} and methane reforming.^{3,4} Thus, studies on the interaction of water with metal surfaces are of fundamental importance for understanding reaction mechanisms. Regarding adsorption, dissociation and desorption of water, many transition metals (e.g. Ru,⁵⁻⁷ Pt,^{8,9} Zr,¹⁰ Ni,¹¹ Pd,¹² Rh,^{13,14} Cu,¹⁵ Ag,¹⁶ and Au¹⁷) have been investigated both experimentally and theoretically. Furthermore, it has been found that co-adsorbed oxygen can induce the dissociation of water on some metal surfaces with hydroxyl groups (OH) as intermediates in the process.¹⁸⁻²² These findings have provided deeper insight into reactions involving water. Ojifinni, Kim, and coworkers found that water can enhance CO oxidation on the Au(111) surface under ultrahigh vacuum (UHV) conditions employing isotopically labeled reactants,^{23,24} and a similar phenomenon has been observed on Pt(111).²⁵ Water enhancement has also been found in CO oxidation on Au/TiO₂^{26,27} and the oxidation of propylene to propylene oxide on Ag(110).²⁸ Additionally, Pan and coworkers noticed that adsorbed water alone or co-adsorbed water and oxygen can induce CO dissociation on Ir(111).²⁹

Although iridium has been investigated widely with respect to its chemical properties³⁰⁻³⁷ due to its high reactivity, the interaction of water with the clean or oxygen modified Ir(111) surface has yet to be a focus of interest. However, Weinberg and coworkers used TPD to investigate the adsorption of water on Ir(110) and found that at most 6% could dissociate at 130 K and hydroxyl formation occurred when water was co-adsorbed with oxygen on Ir(110).³⁸ It is well known that the (111) facet is the most readily formed in classical heat-treated catalysts due to its high stability. Here we present

results demonstrating that water dissociates on the clean Ir(111) surface, and that coadsorbed oxygen can strongly enhance water dissociation via hydroxyl group formation.

EXPERIMENTAL SECTION

All experiments were carried out in an ultrahigh (UHV) vacuum supersonic molecular beam surface scattering apparatus with a base pressure of ~ 2×10^{-10} Torr, which has been described³⁹ in detail previously, but particularly relevant aspects are provided here. This instrument consists of a UHV scattering/analysis section and a differentially-pumped molecular beam generating section. The scattering chamber is equipped with an Auger electron spectrometer (AES), low energy electron diffraction optics (LEED), and a quadrupole mass spectrometer (QMS). The Ir(111) single crystal sample is in the shape of a disk of ~ 1 cm diameter, mounted on a probe which can be adjusted in the X, Y, and Z directions and rotated by a sample manipulator. The Ir(111) sample can be resistively heated to 1550 K and rapidly cooled to 77 K via coupling to a liquid nitrogen (LN₂) bath. A type-C thermocouple (5%-W/Re/26%-W/Re) is spotwelded on the edge of the crystal and employed to measure the sample temperature. Research purity ${}^{16}O_2$ and $H_2{}^{16}O$ were used in this study, as were isotopically labeled D₂O and $H_2^{18}O_1$, to investigate the reaction pathways. All reagents can be delivered to the scattering chamber via molecular beams, which are generated using a system of independent nozzles, each with the same aperture size and separate plumbing to ensure the purity of reagents introduced to the sample surface. The oxygen coverage was determined by LEED measurements on an oxygen saturated surface and the results are in agreement with those that have been reported previously.⁴⁰ Water was dosed via molecular beam on the sample with a flux of ~ 0.08 monolayer (ML)/second and we estimate the surface density of 1 ML water to be ~ 1.23×10^{15} molecules/cm² by analogy

with the water structure on the Pt(111) surface.⁴¹ An inert stainless steel flag is installed in front of the sample for the control experiments to investigate the perturbing effects due to surfaces other than sample, such as the inner walls of the chamber, sample supporting wires, power leads, and the liquid nitrogen cooled sample probe. Periodically, the sample was cleaned by Ar ion sputtering, followed by annealing in gaseous oxygen. More routine cleaning, which must be carried out before every experiment, was performed with several cycles of oxygen adsorption/desorption to remove surface carbon as verified by AES and TPD measurements.

RESULTS AND DISCUSSION

Complete Dissociation of Water on Clean Ir(111)



Figure B.1: TPD spectra of D_2 desorption from D_2O covered Ir(111) with various coverages. Inset graph shows the modified D_2 production with respect to integrated TPD areas of D_2 and HD where the data dots are filled by responding colors. Water was dosed on the surface between 89 and 77 K and the heating rate was 2 K/s.

Complete dissociation of water on the clean Ir(111) surface was investigated by adsorbing water on the clean Ir(111) surface to search for hydrogen formation. We employed isotopically labeled water (D_2O) to eliminate the perturbing effects of background H_2 [due to the thermal dissociation of background H_2O and hydrocarbons (from a small component of fluid vapor from the LN₂ trapped diffusion pump) on hot filaments and diffusion from the stainless steel chamber walls] by monitoring D₂ production from Ir(111), which is one indicator of complete dissociation of water. Therefore, Figure B.1 shows the TPD spectra of D_2 (*m/e* = 4) desorption from Ir(111) covered by D₂O (0 - 2.59 ML) in a broad feature from ~ 200 to 700 K, indicating low temperature water dissociation (< 200 K). The desorption rate of D₂ reached a maximum value at ~ 350 - 400 K, consistent with characteristic features regarding hydrogen desorption from Ir(111).⁴² Compared to the control experiment (we ramped the temperature of the clean sample up to 700 K at the same rate, 2 K/s) shown as the black curve, notable amounts of D₂ are produced from D₂O covered Ir(111) which suggest water dissociation on the clean Ir(111) surface. Additionally, when we dosed water on the inert stainless flag and then conducted TPD measurements, no mass 4 signal was detected, further suggesting that Ir(111) is responsible for water dissociation rather than other surfaces (i.e., copper power leads, tantalum sample-holding wires, and/or thermocouple wires). We estimate that the D_2O dissociation probability increases from ~ 0.004 to 0.016 \pm 0 .0015 with D₂O coverages decreasing from 2.59 to 0.34 ML [we also accounted for mass 3 (HD), which is due to the combination of background H and D from dissociated D_2O . Note that that estimation of water dissociation probability is based on the TPD measurements from saturated hydrogen (1 ML) covered Ir(111), which is difficult to conduct due to the low dissociation probability of hydrogen on Ir(111) (~ 7 \times 10⁻³)⁴² and could be the main source of uncertainty. The inset graph in Figure B.1

represents the modified production of D_2 [i.e., sum of integrated D_2 and half of the HD intensity], initially increasing as a function of increasing D_2O coverages and then leveling off when more than 1 ML of water was adsorbed on Ir(111). This observation is likely due to a decrease in surface active sites which are eventually occupied by absorbed water molecules until fully covering the Ir(111) surface and inhibiting the further dissociation of water.

In order to further study thermal dissociation of water, we investigated the influence of surface temperature by employing molecular beam reactive scattering (MBRS) techniques. We impinged a D_2O beam on Ir(111) at a variety of surface temperatures above that for water desorption (from 300 to 900 K with an interval of 100 K as shown in Figure B.2a) and found that higher surface temperatures produced more D₂, indicating water dissociation on Ir(111) is activated.⁴³ We note that for all temperatures the production of D₂ initially increases to a peak value and then declines until reaching a steady state. The highest intensity is the maximum D2 formation rate (R_{max}) for a given surface temperature. By comparing R_{max} as a function of temperature, an Arrhenius plot has been produced as shown in Figure B.2b resulting in an apparent activation energy for water dissociation (assuming water dissociation is the rate limiting step) on Ir(111) of approximately 170 ± 5 kJ/mol. This is an overall activation energy including the two steps in complete water dissociation: water dissociates to a hydroxyl group and hydrogen atom (H₂O \rightarrow OH + H); the formed hydroxyl group then dissociates to oxygen and hydrogen (OH \rightarrow H + O). By using density functional theory calculations, Mavrikakis et al.⁴⁴ reported that complete water dissociation on Pt(111) has an activation energy barrier of 1.97 eV including 0.88 eV in water dissociation to OH and H and 1.09 eV in OH dissociation, which is comparable to the activation energy we estimate here for Ir(111) (1.97 eV is equal to ~ 190 kJ/mol). Based on the D_2O beam flux and surface

density, we estimate that probabilities for D_2O dissociation during the scattering experiments are in the range ~ 0.0005 to 0.012 corresponding to the temperature range from 300 to 900 K (Figure B.2b). The percentage uncertainty in dissociation probabilities for D_2O has been estimated to be ~ 20 % of the dissociation probability.



Figure B.2: a) Evolution of D_2 from 180 seconds of D_2O impingement on Ir(111) at various temperatures (300 – 900 K). b) Arrhenius plot of maximum D_2 formation rate (R_{max}) regarding the maximum intensity of D_2 (and the probability of D_2O at R_{max}) during reactive scattering experiments at various temperatures.



Figure B.3: Evolution of D₂ from 180 seconds of D₂O impingement on the inert flag (black curve), clean Ir(111) (red curve), 0.06 ML (blue curve) and 0.16 ML O (green curve) pre-covered Ir(111) while the Ir(111) surface temperature was held at 900 K. Oxygen was dosed on the surface between 89 and 77 K.

We selected the experiment with a sample surface temperature of 900 K (shown as the red curve in Figure B.3), to provide additional insights regarding D_2 evolution from water dissociation. Firstly, we carried out a control experiment (see the black curve in Figure B.3) by impinging a D_2O molecular beam (t = 180 s) onto the stainless steel inert flag placed in front of the Ir(111) surface while the temperature was held at 900 K. A negligible amount of D_2 production was observed, suggesting that the catalytic activity for thermal dissociation of water under UHV conditions shown in the red curve is due to the Ir(111) surface. The red curve shows a prompt evolution of D_2 upon exposure to the D_2O beam with the Ir(111) sample held at 900 K. The decline in the evolution of D_2 during the scattering experiment shown as the red curve in Figure B.3 is likely due to an accumulation of oxygen adatoms from water dissociation on Ir(111) eventually reaching an equilibrium between production and desorption of hydrogen and removal of oxygen (oxygen could be abstracted by background CO and replenished by water). To examine this hypothesis, we scattered an equivalent amount of D_2O (the same flux and dosing time of D_2O to that in the experiment shown in the red curve in Figure B.3) on 0.06 and 0.16 ML oxygen pre-covered Ir(111) at 900 K, respectively, as the blue and green curve displayed in Figure B.3. With increasing oxygen coverage, the initial D_2 evolution peak is smaller and gradually decreases with a similar amount of D_2 being observed at steady state (compared to the clean surface), supporting our earlier speculation.

Partial Dissociation of Water on O Pre-Covered Ir(111)

Water dissociation has been observed on many oxygen-modified transition metal surfaces, however, details of the interaction between water and oxygen on the Ir(111) surface have not been reported. In order to study this phenomenon on Ir(111), we coadsorbed oxygen (¹⁶O) with isotopically labeled water (H₂¹⁸O) to search for the scrambled products (indicators of interaction) such as ¹⁸O¹⁶O, ¹⁸O₂ and H₂¹⁶O. Figure B.4 shows TPD spectra of oxygen and water desorbing from the Ir(111) surface in three separate experiments. Firstly, Figure B.4a - 4b display desorption of water and oxygen from 0.30 ML 16 O covered Ir(111) [O₂ is dissociatively chemisorbed on the clean Ir(111) surface ^{45,46}]. As expected no water is observed desorbing but oxygen desorbs from 1000 to 1400 K in agreement with what Weinberg and his colleagues have reported ^{47,48} where they argued that the 1300 K desorption feature is due to iridium oxide [formed at a temperature higher than ~ 700 K on the oxygen covered Ir(111) surface] decomposition. Water TPD spectra on the clean Ir(111) surface display two features as shown in Figure B.5, with one desorption peak at 160 K due to the multilayer adsorption and the other feature at 170 K for the monolayer adsorption. Figure B.4c exhibits only the monolayer desorption feature (170 K) since the Ir(111) surface received a relatively small exposure of isotopically labeled water (0.28 ML). Mass 18 was observed to desorb at 170 K also, which is likely due to $H_2^{16}O$ impurities in the $H_2^{18}O$ sample (Isotec, 95 % ^{18}O) or a mass fragment of $H_2^{18}O$ or water ($H_2^{16}O$) from the background. Notice that there is no oxygen (m/e = 32, 34, 36) desorbing from the Ir(111) surface covered exclusively by water ($H_2^{18}O$), as shown in Figure B.4d. This finding suggests that oxygen atoms from any water dissociation could be totally consumed by reacting with adsorbed trace carbon (from dissociation of hydrocarbon diffusion pump fluid vapor) to form CO and/or CO₂ even on the extremely clean Ir(111) surface, since the low probability of water dissociation (~ 0.012) cannot provide detectable oxygen (monitored by QMS) desorbing in the presence of surface carbon contaminants.

In order to study the interaction of water with oxygen on Ir(111), we added 0.28 ML H₂¹⁸O to 0.30 ML ¹⁶O pre-covered Ir(111) in a temperature range of 89 – 77 K, and then carried out TPD measurements. The results illustrated in Figure B.4e show that a new water desorption feature appears at a higher temperature (235 K). This result likely indicates enhanced water partial dissociation on oxygen covered Ir(111) forming a hydroxyl group (OH) and leading to a high-temperature water desorption feature due to disproportionation ($2OH_a \rightarrow O_a + H_2O_a$) ⁴⁹. Moreover, the notable decrease of the H₂¹⁸O desorption peak at a low temperature (170 K) suggests that most of the adsorbed water has a strong interaction with atomic oxygen on Ir(111) at low temperatures as shown in Figure B.4e. Accordingly, the oxygen TPD spectra in Figure B.4f containing *m/e 32, 34*, and *36* provide evidence regarding oxygen scrambling between oxygen and water also due to disproportionation of formed OH groups. We believe that this process follows the widely accepted mechanism of hydrogen abstraction to produce hydroxyl groups, in which the co-adsorbed atomic oxygen induces water dissociation by abstracting hydrogen atoms from adsorbed water molecules ($O_a + H_2O_a \rightarrow 2OH_a$) ⁴⁹. When we further increase

the $H_2^{18}O$ coverage on 0.30 ML of oxygen pre-covered Ir(111), more recombined water and scrambled oxygen ($^{16}O^{18}O$ and $^{18}O_2$) are produced while the desorption of multilayer water also can be observed with increasing water coverages as shown in Figure B.6.



Figure B.4: TPD spectra of water $(H_2^{18}O \text{ and } H_2^{16}O)$ and oxygen $({}^{16}O_2, {}^{16}O^{18}O \text{ and } {}^{18}O_2)$ from a) and b) 0.30 ML ${}^{16}O$ on Ir(111), c) and d) 0.28 ML $H_2^{18}O$ on Ir(111), and e) and f) 0.28 ML $H_2^{18}O$ on 0.30 ML ${}^{16}O$ pre-covered Ir(111). All species were dosed on the surface at 89 - 77 K. The heating rate during TPD was 2 K/s in the range of 77 - 500 K and 10 K/s in the range of 500 - 1550 K.

We have found enhancement by oxygen adatoms for partial dissociation of water on Ir(111) (see Figure B.4) and also speculated that oxygen from D_2O dissociation could populate the sample surface and block the active sites for further complete dissociation during scattering experiments as shown in Figure B.3. A small amount of water dissociates in the low temperature experiments with the probability ranging from ~ 0.004 - 0.016 and in the molecular beam reactive scattering measurements with probabilities in the range of $\sim 0.0005 - 0.012$, and this suggests that the water dissociation (detected via hydrogen evolution) observed on the clean Ir(111) surface could be due to a small concentration of defects or trace surface carbon contamination whereas clearly a strong interaction between water and oxygen occurs (detected via scrambling) on the (111) terraces. In order to investigate the effect of carbon, we dosed propylene on the clean Ir(111) surface via molecular beam and then heated the sample to 900 K to obtain ~ 4.5 times more carbon on Ir(111) than the "clean" surface. However, D₂O scattering experiments on carbon pre-covered Ir(111) showed that only 10 % larger peak value of D_2 was detected than that on the clean surface, indicating carbon is not likely responsible for water dissociation. Although more D₂ production has been observed on carbon precovered surface during the steady state, we believe that it is because the rate of O blocking active site (i.e. defects) has been decreased by CO oxidation which can consume oxygen atoms and suppress their population on Ir(111). Therefore, we suspect that water dissociation on the clean Ir(111) surface is mediated by defects⁴⁹ (the water dissociation probability on Ir(110) is ~ $6\%^{38}$). The defective sites are likely blocked by oxygen atoms from dissociated water causing the attenuation of further dissociation and evolution of D_2 . On the other hand, oxygen atoms can enhance partial dissociation of water on the (111) terraces of our iridium sample via abstraction of H. Additionally, complete dissociation of D_2O on defects of Ir(111) might result in the desorption of D_2 at the

higher temperatures (up to ~ 600 K) shown in Figure B.1, compared to the D_2 TPD spectra reported by Engstrom and Weinberg (hydrogen and deuterium desorption features are identical and end at ~ 500 K on Ir(111) terraces⁴²). The broader TPD spectra for deuterium in our work could be due to the different source for D_2 , i.e., produced from water dissociation whereas Weinberg and his co-workers directly adsorbed deuterium for their TPD measurements.



Figure B.5: TPD spectra of H₂¹⁶O desorption from various water coverages on Ir(111). Water was dosed on the surface between 89 and 77 K and the heating rate was 2 K/s.

Comparing the probability of water dissociation in TPD (0.004 - 0.016 \pm 0.0015) and scattering (0.0005 - 0.012 with a percentage uncertainty of 20 %) experiments, we have noted that slightly larger fractions of D₂O molecules can completely dissociate on the clean Ir(111) surface in TPD. Since the adsorption probability is likely only affected in a minor way by surface temperature,³⁰ the difference in water dissociation probability for the two types of measurements (TPD and MBRS) might be due to the residence time of the molecules. The longer residence time of water molecules at low temperature
(approaching infinity at 77 K) in TPD allows D_2O molecule to diffuse to active sites and dissociate with a large number of attempts. As a result, a higher probability of reaction is obtained. In contrast, in the scattering experiments with surface temperatures much higher than that of water desorption a much shorter residence time (ranging from $10^{-6} - 10^{-11}$ seconds) is expected so that water molecules cannot repeatedly reach the reactive sites since desorption is quite rapid, and this results in a comparably lower dissociation probability. However, reactivity increases with increasing surface temperature when a D_2O molecular beam is impinged on Ir(111), indicating that complete dissociation of water is thermally activated at temperatures above 300 K and mainly influenced by reaction probability rather than probability of molecules arriving at the defective sites. Additionally, a crude calculation of D_2O coverage shows it to be very small ($10^{-7} - 10^{-12}$ monolayer) during the scattering experiments with the temperatures ranging from 300 – 900 K.

The role of a trace amount of moisture in increasing reaction rates in high surface area catalysis, has been identified in investigations regarding CO oxidation²⁶ and propylene epoxidation⁵⁰ on supported gold clusters. The data presented here aim to reinforce the understanding of the role of adsorbed water with clean and oxygen modified Ir(111).



Figure B.6: TPD spectra of $H_2^{16}O$ desorption from a) various $H_2^{16}O$ coverages on Ir(111) and $H_2^{18}O$ desorption from b) various $H_2^{18}O$ coverages on 0.30 ML of ¹⁶O pre-covered Ir(111). All species were dosed on the surface at 89 - 77 K and the heating rate during TPD was 2 K/s.

CONCLUSIONS

In summary, water dissociation has been observed on the clean Ir(111) surface via TPD with a small dissociation probability (lower than ~ 0.016 ± 0.0015). By using molecular beam reactive scattering techniques, we found that water dissociation on Ir(111) is activated whereas adsorbed oxygen produced from the reaction can occupy the active sites to inhibit the further dissociation of water causing dissociation probabilities in a range of ~ 0.0005 - 0.012 (percentage uncertainty is 20 %) at the maximum reaction

rate. Furthermore, the apparent activation energy has been estimated to be approximately 170 ± 5 kJ/mol, which may not be applicable to the higher coverages employed for the TPD measurements. When water and oxygen were co-adsorbed on Ir(111), scrambled products were detected, suggesting that oxygen can induce partial dissociation of water on Ir(111) and recombinative desorption in which hydroxyl groups are considered to be likely intermediates. A new prominent desorption feature at 235 K, which is at a much higher temperature than the characteristic desorption feature for monolayer water on clean Ir(111) (170 K), suggests a strong interaction between oxygen and water.

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