Model Studies with Gold: A Versatile Oxidation and Hydrogenation Catalyst

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CONSPECTUS

Historically, scientists have considered gold an inert catalyst constituent. However, in recent decades, chemists have discovered that nanoscale gold shows exceptional activity for many chemical reactions. They have investigated model gold surfaces in order to obtain fundamental understanding of catalytic properties. In this Account, we present our current understanding of oxidation and hydrogenation reactions on the Au(111) single crystal as a planar representative of gold catalysts, revealing the interesting surface chemistry of gold.

We begin by comparing two inverse reactions, alcohol oxidation and aldehyde hydrogenation, on a Au(111) surface. Beyond the expected different chemistry, we observe intriguing similarities since the same surface is employed. First, both molecular oxygen and hydrogen have high barriers to dissociation on Au(111), and frequently chemists study reactions here by using atomic O and H to populate the surfaces. Recombinative desorption features of oxygen and hydrogen are apparent at ~500 and ~110 K, lower than other transition metals. These results indicate that oxygen and hydrogen have low desorption activation energies and weakly chemisorb on the surface, likely leading to selective reactions. On the oxygen-precovered Au(111) surface, alcohols are selectively oxidized to aldehydes. Similarly, weakly bound hydrogen atoms on Au(111) also show chemoselective reactivity for hydrogenation of propionaldehyde and acetone.

The second similarity is that the gold surface activates self-coupling of alcohol or aldehyde with oxygen or hydrogen, resulting in the formation of esters and ethers, respectively, in alcohol oxidation and aldehyde hydrogenation. During these two reactions, both alkoxy groups and alcohol-like species show up as intermediates, which likely play a key role in the formation of coupling products. In addition, the cross coupling reaction between alcohol and aldehyde occurs on both O- and H-modified surfaces, yielding the production of esters and ethers, respectively. Thus, we can tune the molecular structure of both esters and ethers by selecting the corresponding aldehyde and alcohol for the coupling reaction.

These studies indicate that gold is a versatile active catalyst for various reactions, including oxidation and hydrogenation transformations. Despite the very different chemistry for these two reactions, we can establish an intrinsic relationship due to the distinct catalytic properties of gold. It can show activity for selective reactions on both O- and H-covered Au(111) and further induce the coupling reaction between surface reactants and adsorbed O/H to produce esters and ethers. This comparison demonstrates the unique surface chemistry of gold and enhances understanding of its catalytic properties.

1. Introduction

Over much of human history, gold has been a highly sought-after precious metal. One of the important reasons is that gold has been considered to be catalytically inert to chemical reaction.[1] Hammer and Norskøv's seminal theoretical work on H₂ dissociation on gold indicated that two factors are related to its' nobleness, a high degree of filling of the antibonding states on adsorption and orbital overlap with the adsorbate. Both lead to weak absorbate−metal interactions and the high energy barrier for dissociation.[1]

However, pioneering work by Haruta,[2] Bond,[3] and Hutchings[4] found that gold nanoparticles have high activity

for CO oxidation, 1,3-butadiene hydrogenation, and hydrochlorination of acetylene, respectively. Currently, supported gold-based catalysts have been extensively investigated showing activity in a wide range of reactions, including oxidation and hydrogenation.[5−8] A fundamental understanding of relevant reaction mechanisms and catalytic properties is highly desirable, especially for the determination of active sites, such as exposed facets on nanoparticles, low coordinated sites, and interfaces between metal particles and supports. Among them, on thermally pretreated gold catalysts, the {111} facet is the most stable and prevalent exposed surface. Therefore, many studies have been conducted on Au(111) single crystal surfaces in order to collect mechanistic information for better understanding of gold catalytic activity.

In this Account, we compare fundamental studies regarding two types of reactions on the Au(111) surface, oxidation and hydrogenation. Alcohol oxidation and carbonyl hydrogenation reactions are two of the most important organic transformations and have been widely used in bulk and fine chemical preparations (Scheme 1). Molecular oxygen and hydrogen gas are considered as the most attractive oxidant and reductant, respectively, due to their low cost and minimal byproduct formation. In addition, oxidative

and reductive self- or cross-couplings between alcohols and aldehydes serve as direct and economical ways to prepare esters and ethers. The gold model surface has been found to be active for alcohol oxidation and aldehyde hydrogenation but different intermediates are observed, which further lead to different coupling reactions with production of esters and ethers on oxygen and hydrogen precovered surfaces, respectively. These studies indicate that gold is a versatile catalyst for both oxidation and hydrogenation, in which adsorbed oxygen and hydrogen result in dissimilar surface chemistry. This Account describes the nature of gold surface chemistry by comparing oxidation and hydrogenation reactions on the model surface.

2. Oxygen and Hydrogen Desorption from Au(111)

Gold catalysts have been identified as highly active for many oxidation reactions, such as CO oxidation,[9,10] the water gas shift reaction,[11] and selective oxidation of alcohols.[12] In order to explore reaction mechanisms, model gold surfaces have been empolyed.[13−15] Furthermore, gold catalysts have also been found to be active for hydrogenation reactions, particularly for selective hydrogenation transformations.[16−18] We have conducted fundamental studies regarding hydrogenation reactions on a model Au(111) surface in order to provide insights into related reaction mechanisms on classical gold-based catalysts.[19−25]

Friend and co-workers found a high barrier for molecular oxygen dissociation on Au(111), and the probability is extremely low, much less than 10^{-6}.[26] Thus, atomic oxygen is frequently produced and deposited on the gold surfaces for study of oxidation reactions. Figure 1 shows temperature-programmed desorption (TPD) spectra of oxygen and

SCHEME 1. Alcohol Oxidation and Carbonyl Hydrogenation Reactions
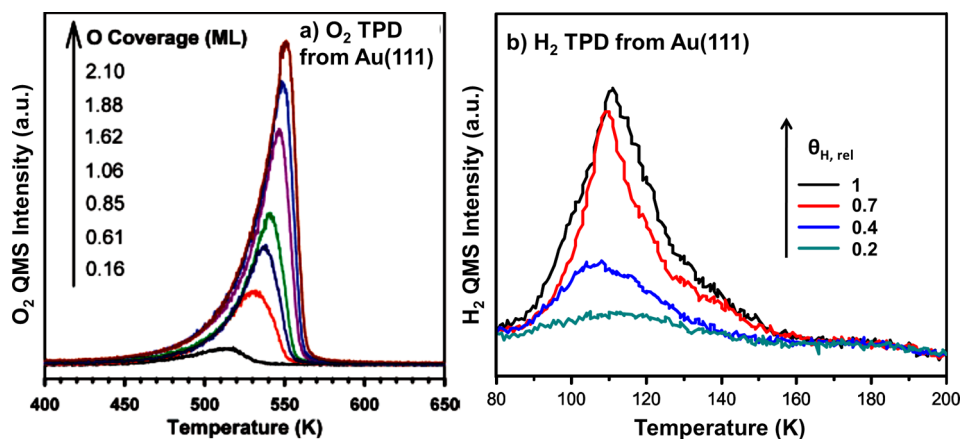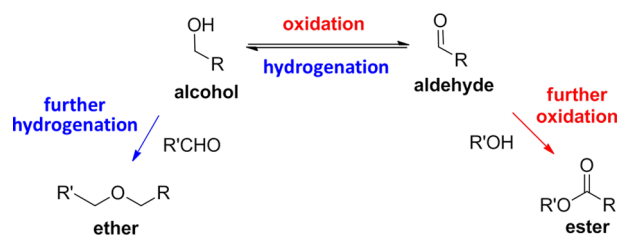
FIGURE 1. Desorption of (a) oxygen[27] and (b) hydrogen[21] from Au(111). Reproduced with permission. Copyright 2008 and 2011 American Chemical Society.
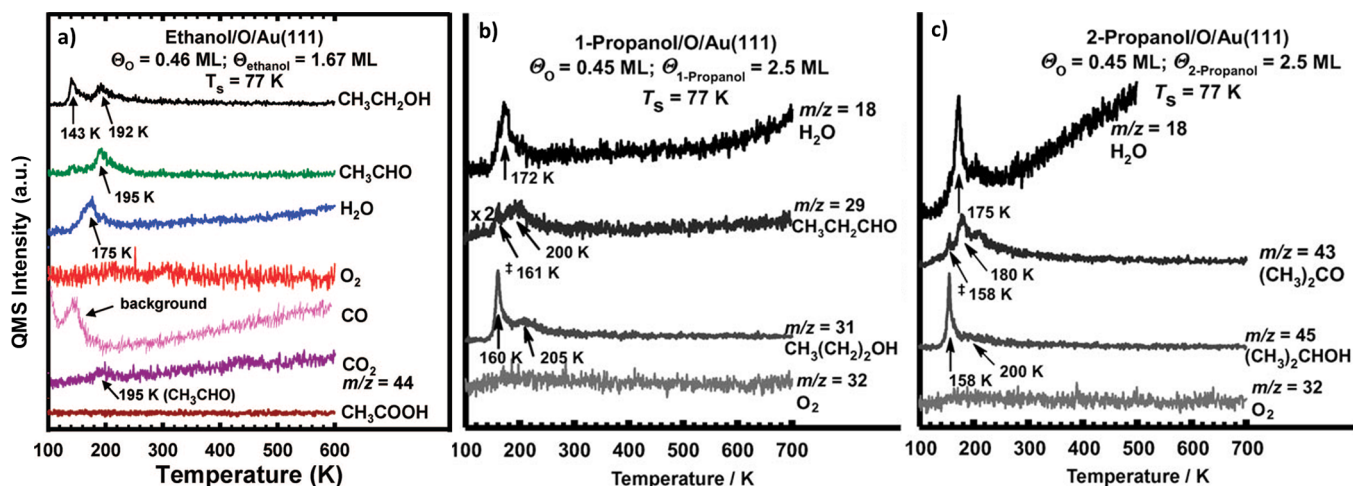
FIGURE 2. Oxidation of (a) ethanol,[32] (b) 1-propanol,[33] and (c) 2-propanol[33] on oxygen covered Au(111). Reproduced with permission. Copyright 2008 American Chemical Society and John Wiley and Sons.

hydrogen from a clean Au(111) surface.[27] In these experiments, atomic oxygen was prepared by a radio frequency generated plasma source and deposited on the metal surface at a low temperature, $\sim$77 K. A monolayer (ML) of atomic oxygen was estimated to yield a surface density of 3.93×10^{14} O atoms/cm^2. A full range of oxygen coverages can be estimated based on the integrated area under the corresponding TPD spectra.[27]

Upon heating of the sample, oxygen recombinatively desorbs from Au(111) with a peak at $\sim$540 K (Figure 1a), in agreement with results collected by Saliba, Parker, and Koel.[28] They adsorbed atomic oxygen on a clean Au(111) surface by exposing to ozone (O$_3$) at 300 K.[28] Friend and co-workers employing scanning tunneling microscopy (STM) showed that oxygen deposition causes gold atoms to release from the Au(111) herringbone structure yielding a roughened surface with the formation of Au—O clusters.[29] Note that oxygen desorption from Au(110) is apparent at a higher temperature, $\sim$590 K.[8]

Similar to oxygen, molecular hydrogen cannot readily dissociate on model gold single crystal surfaces. Sault, Campbell, and Madix employed a hot filament to thermally dissociate molecular hydrogen and deposited H atoms on a Au(110) surface. Their TPD measurement showed H$_2$ desorption with a single feature centered at 216 K.[30]

Recently, we studied hydrogen adsorption and desorption on the more close-packed Au(111) surface, using a homemade thermal hydrogen cracker to prepare atomic hydrogen.[21] Figure 1b illustrates the desorption of hydrogen from H/Au(111), in which the relative coverages of hydrogen ($\theta_{H,rel}$) were determined by comparing integrated areas under TPD spectra to the integral for the saturated surface.

The results of thermal desorption measurements showed that with increasing H relative coverages, hydrogen yield desorption features peaked in a small temperature range from 108—111 K suggesting first-order desorption kinetics. Based on the Redhead approximation, the apparent desorption activation energy of hydrogen from Au(111) was estimated to be $\sim$28 kJ/mol. This low desorption activation energy for H$_2$ indicates that H atoms weakly adsorb on the Au(111) surface, which likely induces unique surface chemistry. In addition, a much higher activation energy (51 kJ/mol) for H$_2$ desorption has been observed on Au(110),[30] a more corrugated surface, indicating structural sensitivity.

DFT calculation results indicate that H atoms preferably adsorb on fcc hollow sites.[24] There is a small barrier (0.07 eV) for weakly chemisorbed H atoms to diffuse to hcp hollow sites, strongly suggesting that the surface-bound atoms may be able to randomly move on the surface at low temperatures. However, H$_2$ formation requires the atoms to diffuse to the atop site on Au(111). The formation of H$_2$ by two adjacent atop-bound H atoms is barrierless and exothermic by over 0.75 eV. Thus, the total H$_2$ desorption activation energy only accounts for the diffusion of H atoms from fcc hollow to atop sites, which is calculated to be $\sim$0.29 eV (28 kJ/mol), consistent with our TPD results.[21]

3. Alcohol Oxidation and Aldehyde Hydrogenation on Au(111)

3.1. Alcohol Oxidation on Au(111). Alcohols are typically coadsorbed on the atomic oxygen-precovered Au(111) surface to investigate the reaction mechanism. Early work on methanol oxidation suggested that only CO and CO$_2$ are produced during the reaction with no other partial oxidation
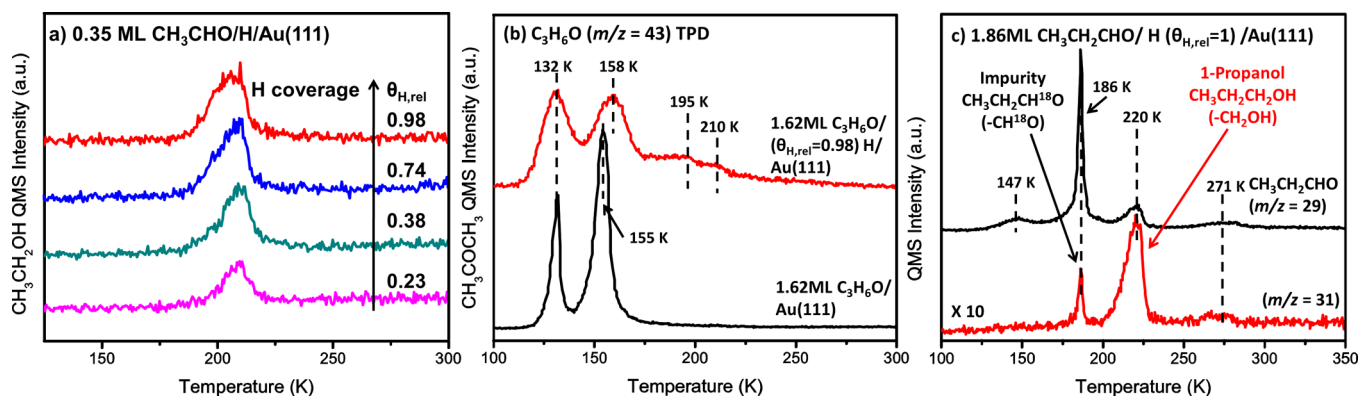
FIGURE 3. Hydrogenation of (a) acetaldehyde,[21] (b) acetone,[23] and (c) propionaldehyde[23] on hydrogen covered Au(111) surfaces. Reproduced with permission. Copyright 2011 American Chemical Society and 2012 John Wiley and Sons.

products or derivatives such as formaldehyde, formic acid, or methyl formate being generated.[27,31]

In contrast, selective oxidation has been observed when longer chain alcohols were employed. Figure 2 shows oxidation of ethanol, 1-propanol, and 2-propanol on Au(111), selectively yielding acetaldehyde, propionaldehyde, and acetone, respectively. Figure 2a illustrates TPD spectra of ethanol oxidation. A selectivity of 100% toward acetaldehyde was measured along with water production. An isotopically labeled experiment was also performed and indicated the lack of β-C−H cleavage. Thus, the formation of acetaldehyde is likely via the cleavage of both α-C−H and O−H bonds.[32]

We also compared oxidation of 1-propanol and 2-propanol on Au(111). As shown in Figure 2b,c, 1-propanol and 2-pronaol are selectively oxidized to propionaldehyde and acetone, respectively, at low temperatures (less than 300 K). No other products were detected. The activation energies for partial oxidation of 1-propanol and 2-propanol were estimated to be 2.8 ± 3.1 and 1.6 ± 1.9 kJ/mol, respectively.[33] The cleavage of the α-C−H bond was also considered to be the key step.

However, there is a new wrinkle regarding the surface chemistry of Au(111) and alcohol oxidation according to the elegant studies by Friend and co-workers.[34] In addition to the production of aldehydes, they also observed a self-coupling reaction for ethanol producing the corresponding ester and ethyl acetate. This reaction was also observed during the methanol oxidation reaction, yielding the production of methyl formate.[35] This esterification reaction was not initially observed by Gong and Mullins in their study.[32] Friend et al. suggested that there are two significantly different reaction conditions that could affect the experimental results: (1) the method for depositing atomic oxygen

species that leads to difference surface reactivity; (2) the surface temperature at which adsorbents deposited.[34] Gong and Mullins have since also found the production of ethyl acetate on Au(111) at low oxygen precoverages.

3.2. Aldehyde Hydrogenation on Au(111). In order to better understand gold catalytic activity, the inverse reaction of alcohol oxidation, aldehyde hydrogenation, was investigated. The first hydrogenation study completed involved acetaldehyde conversion to ethanol.[21] Upon heating adsorbed acetaldehyde on the H precovered Au(111) surface, the desorption of ethanol was observed, yielding a peak at 210 K, as shown in Figure 3a. The effect of varying hydrogen coverage was also investigated showing increasing H coverages can promote the production of ethanol. In addition, acetaldehyde was observed to polymerize on the clean surface, similar to other transition metals such as Pd,[36] Ru,[37] Cu,[38] and Ag.[39] This phenomenon is probably related to the desorption of acetaldehyde during the hydrogenation reaction, which shows significant changes compared with desorption from clean Au(111). Further studies such as computational modeling and vibrational spectroscopy are needed for a better understanding of the reaction mechanisms.[21]

Probe reactions regarding the hydrogenation of other carbonyls have also been investigated. Acetone and propionaldehyde, as isomers, were studied, and the reactivity was compared in order to obtain an enhanced understanding of hydrogenation on Au(111).[23] Figure 3b illustrates TPD measurements of acetone on clean and H coadsorbed Au(111) surfaces. Acetone (1.62 ML) was absorbed on Au(111), resulting in desorption of monolayer and second-layer molecules, at 155 and 132 K, respectively.[40] In contrast, coadsorption of acetone and H can cause a significant transformation for acetone thermal desorption, with broader

monolayer and second-layer desorption features, and two new desorption features become apparent at higher temperatures, at 195 and 210 K. Although those observations indicate a strong interaction between acetone and H adatoms on Au(111), no hydrogenated products such as 2-propanol were detected.

Propionaldehyde, a constitutional isomer of acetone with the carbonyl group on a terminal carbon atom, was studied in order to collect more mechanistic information regarding hydrogenation of C=O groups on Au(111).[23] This can be considered as an inverse process of 1-propanol oxidation on O/Au(111) as discussed above. On the clean surface, propionaldehyde has a monolayer desorption feature at ~154 K and a multilayer desorption feature at ~121 K. Additionally, there is another desorption peak at higher temperatures, ~270 K, due to the aldehyde polymerization, similar to acetaldehyde.[21] Figure 3c shows TPD spectra following coadsorption of propionaldehyde and H on Au(111). The thermal desorption of propionaldehyde ($m/z = 29$) showed several changes, including two small features at 147 and 220 K, and a strong and sharp feature at 186 K. Meanwhile, the desorption features from surface polymers remained at 271 K. These changes indicate a strong interaction, leading to the formation of 1-propanol, which desorbs at 220 K as shown by signals for mass 31, a major mass fragment of 1-propanol. In addition, CH_3CH_2CHO also has a mass fragment for $m/z = 31$, which is a very small fraction and can mirror the desorption spectra of mass 29, yielding a feature at 186 K. However, it was estimated that 90% of the mass 31 desorption peak at 220 K is from 1-propanol.[23]

It is apparent that there is different reactivity for acetone and propionaldehyde hydrogenation on Au(111). Two factors were considered to be associated with this result. First, DFT calculations indicate different energetic barriers for these two reactions.[23] Both acetone and propionaldehyde have a barrier of 0.2 eV for the first hydrogenation step of adding a H atom on the carbonyl-carbon atom and forming a covalent bond with a surface gold atom as an alcohol-like intermediate. However, the acetone intermediate has a lower barrier for returning the H atom to the surface than the step for taking the second H atom to form 2-propanol. In contrast, a lower barrier for the second H addition was observed with propionaldehyde hydrogenation.[23] This finding suggests that once it forms the partially hydrogenated intermediate on the surface (from the first H reaction), the acetone intermediate favors reversing back to produce adsorbed acetone whereas the propionaldehyde intermediate is likely to add the second H atom to provide 1-propanol.

The second possible factor is related to polymerization. DFT calculations and TPD measurements indicate that propionaldehyde favors polymerization on the H-covered surface whereas no such phenomenon was observed for acetone. The polymerization of propionaldehyde yields strongly bound molecules on the surface, indicated by desorption at a higher temperature as shown in Figure 3c. This allows propionaldehyde to remain on Au(111) at higher temperatures, which increases the reaction probability. Combined, those two factors help explain the surface chemistry for chemoselective hydrogenation of acetone and propionaldehyde on gold.[23]

4. Coupling Reactions for Production of Esters and Ethers on Au(111)

4.1. Ester Formation via Alcohol Coupling. As discussed above, Friend and co-workers found a series of alcohol self-coupling reactions assisted by adsorbed atomic oxygen on the Au(111) surface producing the corresponding esters. This reaction is facile and occurs below 300 K on Au(111) for both methanol and ethanol self-coupling. However, the selectivity for producing aldehyde versus ester is strongly dependent on the concentration of surface oxygen.[34,35] During the oxidation of methanol, the esterification only occurs at low coverages of oxygen (below 0.5 ML) and the selectivity for ester monotonically decreases with increasing oxygen coverages.[35] The activity of the ethanol self-coupling reaction reaches the highest value at an oxygen coverage of 0.2 ML (in a range from 0.05 to 1.0 ML).[35] Vibrational spectroscopy measurements indicate that methoxy and ethoxy groups are important reaction intermediates for the formation of methyl formate and ethyl acetate, respectively.[34,35]

Self-coupling of alcohols on oxygen-covered Au(111) has been proposed to occur via a reaction between the surface intermediate alkoxy group and the produced surface bound aldehyde. Therefore, studies on cross-coupling reactions have been further investigated.[41] Figure 4 shows results for methanol and aldehyde sequentially deposited on Au(111) with preadsorption of 0.05 ML of atomic oxygen. The methoxy group is formed on the surface via the partial oxidation of methanol and subsequently reacts with the adsorbed aldehyde. Four different aldehydes have been tested including formaldehyde, acetaldehyde, benzaldehyde, and phenylacetaldehyde, selectively yielding the corresponding methyl esters. Note that no methyl formate was detected, indicating the low selectivity for self-coupling of methanol during these reactions. Isotopic labeling studies demonstrate that the methoxy group remains intact during
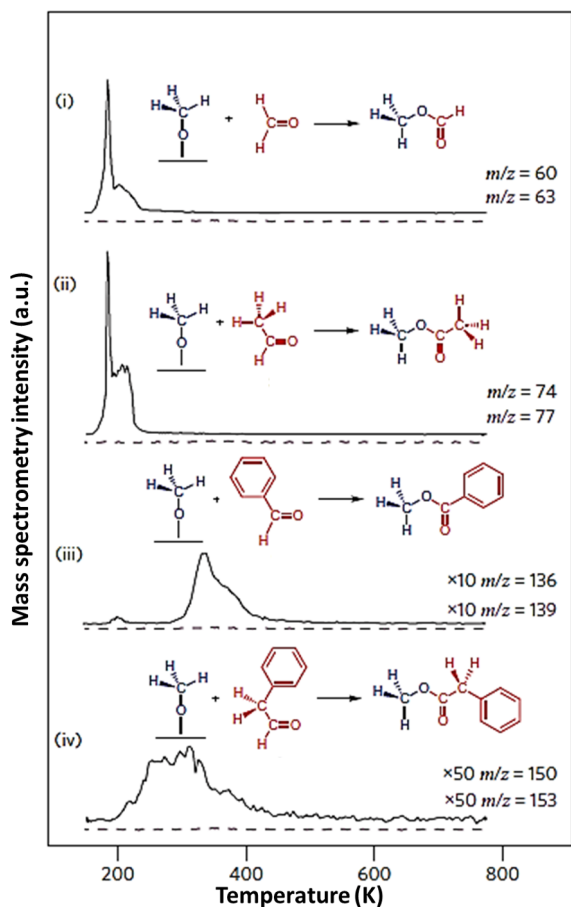
FIGURE 4. Coupling reaction of alcohol and aldehyde to produce esters on oxygen covered Au(111) as discovered by Friend and co-workers.[41] Reproduced with permission. Copyright (2010) Nature Publishing Group.

FIGURE 5. Schematic diagram of alcohol−aldehyde coupling reaction on Au(111).[42]

the coupling reactions and the H from the α-carbon in the aldehydes is released to form the methyl esters.[41]

The self-coupling reaction mechanism illustrated in Figure 5 has been proposed.[42] Step a shows the adsorption of alcohol on Au(111), which further interacts with oxygen adatoms resulting in the formation of an alkoxy surface species (step b). DFT calculations based on methanol self-coupling suggest that the reaction between methanol and oxygen to form methoxy and an adsorbed OH has a significantly lower barrier (0.41 eV) than the dissociation of methanol on the surface (1.58 eV), clearly demonstrating the importance of surface oxygen atoms. The methoxy group further reacts with oxygen to produce formaldehyde via the β-H elimination mechanism (step c) with a noticeable barrier of 0.49 eV. Steps d and e illustrate the coupling reaction via nucleophilic attack of the alkoxy intermediate to aldehyde, leading to the production of ester. Note that for both steps b and e, oxygen atoms on the surface promote the release of H from the alcohol and coupling intermediate

to form the alkoxy group and ester product. Theoretical modeling of the methanol self-coupling reaction indicated that the formation of aldehyde has the highest barrier, suggesting that it is the rate-limiting step.[41,42]

The self-coupling reaction of alcohol has also been investigated on nanostructured gold catalysts. Wittstock and co-workers prepared nanoporous gold (np-Au) catalysts by using nitric acid to leach Ag from AuAg alloys. This material has been employed to study ester production via methanol oxidative self-coupling.[43,44] Catalytic testing has been performed in a flow reactor with a monolithic np-Au disk at ambient pressure and with temperatures lower than 100 °C. At room temperature (20 °C), the methanol conversion has been found to be ∼10%, but the selectivity toward methyl formate (desired product) was close to 100%. With increasing temperature to 80 °C, the selectivity only slightly reduced to 97% whereas the conversion of methanol was significantly enhanced to 60%. This catalyst also showed excellent stability; the activity remained constant for more than 7 days at the mild reaction conditions with a low temperature of 30 °C.[44] The activation energy of ester formation has been estimated to be 70.6 kJ/mol, lower than the combustion of methanol to CO_2 (99.8 kJ/mol).[44] Note that the effect of Ag in np-Au has also been investigated since their previous work indicated that residual Ag can activate molecular oxygen. The experimental results showed that the addition of Ag in the catalyst decreases the selectivity for partial oxidation via promoting CO_2 production.[44]

The work of Wittstock and co-workers clearly shows that nanoporous gold catalysts have extraordinary activity for
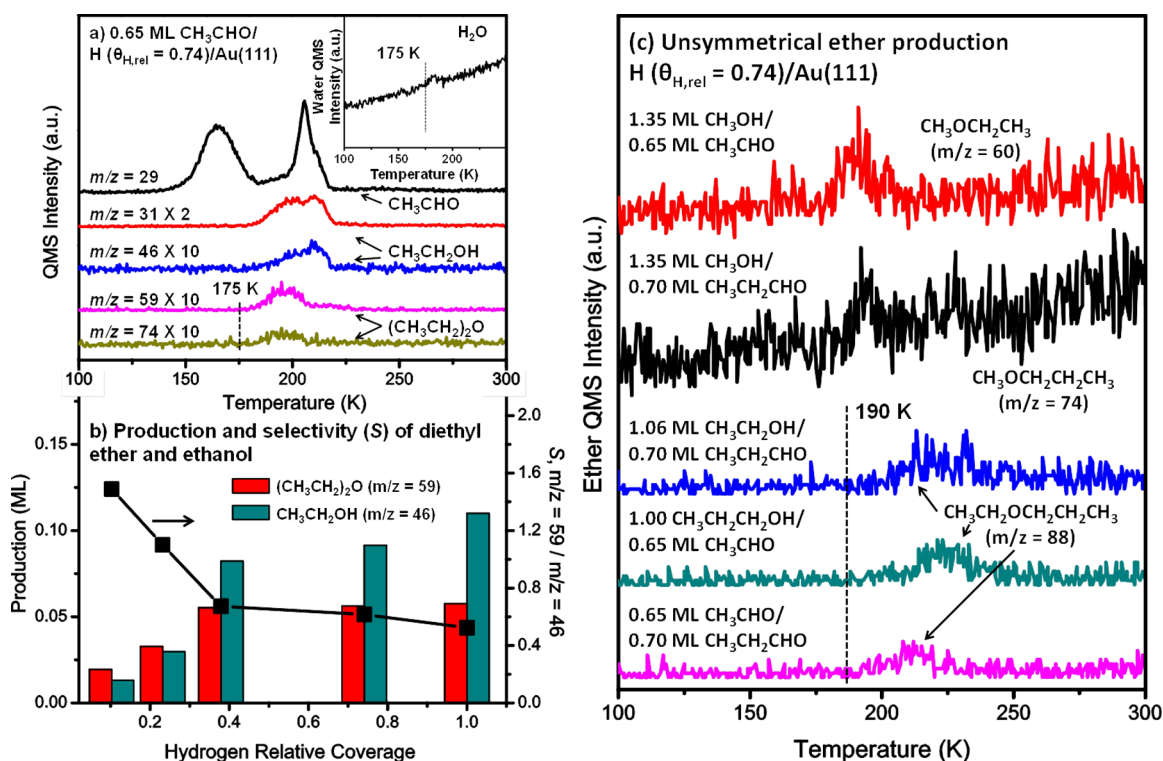
FIGURE 6. (a) Reactions of acetaldehyde with H atoms on Au(111). (b) Comparison of the selectivity of ethanol and diethyl either. (c) Ether production via reductive coupling of aldehyde–aldehyde and aldehyde–alcohol on H covered Au(111).[20] Reproduced with permission. Copyright 2012 American Chemical Society.

esterification reactions via the oxidative self-coupling of methanol, in good agreement with the study of Friend et al. on a model Au(111) single crystal surface. This is a very good example how the information collected from model catalysis studies under ultrahigh vacuum conditions can be transferred to more practical catalytic systems in ambient conditions.[45]

4.2. Ether Formation via Aldehyde Coupling. The conversion of aldehyde to alcohol on H/Au(111) has been observed with acetaldehyde and propionaldehyde. However, as was discussed regarding oxidation reactions, there is another reaction channel for adsorbed aldehydes on H covered Au(111).[20] Figure 6a illustrates the TPD spectra from a surface coadsorbed with H and acetaldehyde. Based on the discussion in section 3.2, acetaldehyde can be hydrogenated to ethanol.[21] Further, desorption features for masses 59 and 74 were detected starting at 175 K and reached a peak value at 190 K. These large mass fragments indicate the production of diethyl ether. In addition, water was produced, suggesting a self-coupling reaction of acetaldehyde toward diethyl either on the hydrogen covered gold surface: $2CH_3CHO + 2H \rightarrow (CH_3CH_2)_2O + H_2O$.[20]

The effect of H coverage on the distribution of products, ethanol and diethyl ether, was investigated. Figure 6b

indicates that increasing hydrogen coverage promotes the production of both ethanol and diethyl ether. Furthermore, high H coverage leads to low selectivity toward ether production whereas more ethanol is produced. A blank experiment showed that coadsorbed ethanol and aldehyde on the clean Au(111) surface cannot initiate a reaction to produce diethyl ether. In addition, no ether production was observed via ethanol coupling on the H covered surface. These results strongly suggest that both H and acetaldehyde are indispensable for ether production. DFT calculations showed that aldehyde hydrogenation on Au(111) has a partially hydrogenated alcohol-like intermediate, which likely plays a key role in the acetaldehyde self-coupling reaction and ether production. High H coverages enhance full conversion of acetaldehyde to ethanol. Thus, as H adatoms are depleted, acetaldehyde and produced ethanol alone are not able to induce ether production. In contrast, low H coverages favor partial hydrogenation to produce alcohol-like intermediates, which further react with acetaldehyde to form diethyl ether. Note that similar results are also observed for the reaction between propionaldehyde and H on Au(111), in which di-*n*-propyl ether is produced and low H coverages result in higher ether selectivity.[20] Those findings suggest a homocoupling

reaction of aldehydes on H covered Au(111) to produce symmetrical ethers.

On the other hand, unsymmetrical ethers can also be synthesized via a similar reaction mechanism on the Au(111) surface. Figure 6c shows TPD spectra from the H-covered surface upon coadsorption of aldehydes and alcohols with different chain lengths. Figure 6c indicates that unsymmetrical ethers can be produced via cross-coupling reactions between corresponding alcohols and aldehydes. For example, methanol reacts with acetaldehyde or propionaldehyde on H/Au(111), respectively, producing methyl ethyl ether and methyl propyl ether. Furthermore, it was observed that ethyl propyl ether can be synthesized via three different reactions: ethanol with propionaldehyde, 1-propanol with acetaldehyde, and acetaldehyde with propionaldehyde. These experimental results demonstrate a synthesis method for producing unsymmetrical ethers via a cross-coupling reaction with corresponding aldehyde−aldehyde or aldehyde−alcohol. Note that during these reactions, self-coupling of a single aldehyde has also been detected (e.g., diethyl ether was observed from H/Au(111) with coadsorption of methanol and acetaldehyde). There is no clear indication which product, symmetrical or unsymmetrical ether, is more favorable to be produced. More studies are needed to explore the relationship between selectivity for two types of coupling reactions and surface reactant concentration.[20]

As Figure 7 shows, two mechanisms are proposed for both cross-coupling reactions of aldehyde−aldehyde and aldehyde−alcohol, illustrated by paths 1 and 2, respectively. Aldehydes absorb on a metal surface with the η^1(O) configuration as shown in step a, in which the aldehyde oxygen interacts with the surface via a lone pair of electrons. Based on DFT calculations, the aldehyde can be partially hydrogenated to form an alcohol-like surface intermediate (step b), which further interacts with an adsorbed aldehyde molecule with the assistance of H adatoms to generate ether and the byproduct water as shown by steps c−f. In isotopic experiments with the deuterium covered surface, acetaldehyde and propionaldehyde yield the production of $(CH_3CHD)_2O$ and $(CH_3CH_2CHD)_2O$, respectively, in agreement with the proposed mechanism for adding H to the α-carbon for ether formation. In path 1, symmetrical ethers are produced if the R and R′ groups are the same. Otherwise, unsymmetrical ethers will be synthesized. In addition, path 2 demonstrates the reaction pathway for coupling between aldehyde and alcohol for the production of ethers, which is very similar to the mechanism for the aldehyde−aldehyde
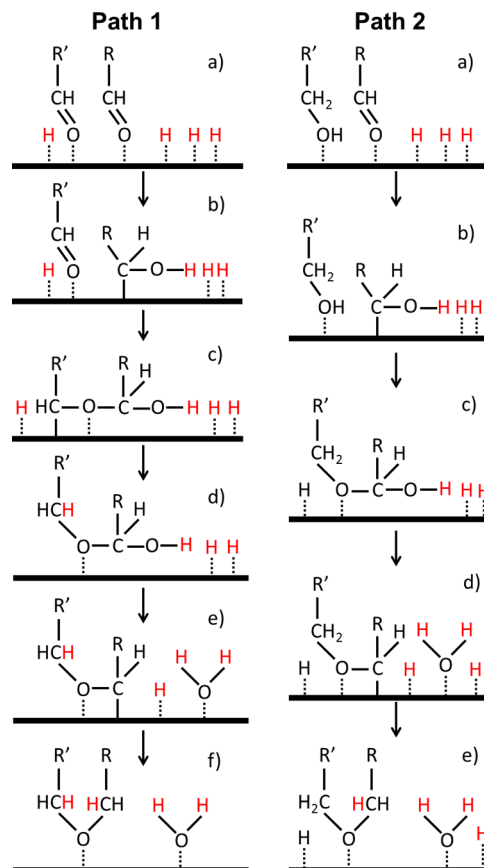

FIGURE 7. Schematic diagram of ether production on Au(111) from coupling of aldehyde−aldehyde (path 1) and aldehyde−alcohol (path 2).[20] Reproduced with permission. Copyright 2012 American Chemical Society.

reaction in path 1. The only difference is that the formed surface intermediate directly interacts with adsorbed alcohol on H/Au(111) to produce ethers. This study reveals a heterogeneous catalytic method for tunable ether synthesis on a model gold surface via a coupling reaction by selecting the proper corresponding aldehydes and alcohols.[20]

Furthermore, the ether production via alcohol/aldehyde coupling has also been discovered by Milone and co-workers from cinnamaldehyde hydrogenation on TiO_2-supported gold nanoparticle catalysts. This experiment has been conducted in ethanol at 333 K with 1 atm of hydrogen pressure. As depicted in Figure 8, three main products have been observed during the reaction: hydrocinnamaldehyde (HCA), cinnamyl alcohol (UA), and cinnamyl ethyl ether (CEE). The first two products are formed via the direct hydrogenation, and the latter is due to the coupling reaction between cinnamaldehyde and ethanol. Figure 8b shows the effect of selectivity on catalysts with different pretreatments. Au/TiO_2, Au/TiO_2[LTR (low temperature reduced)] and Au/TiO_2[HTR (high temperature reduced)] represent the
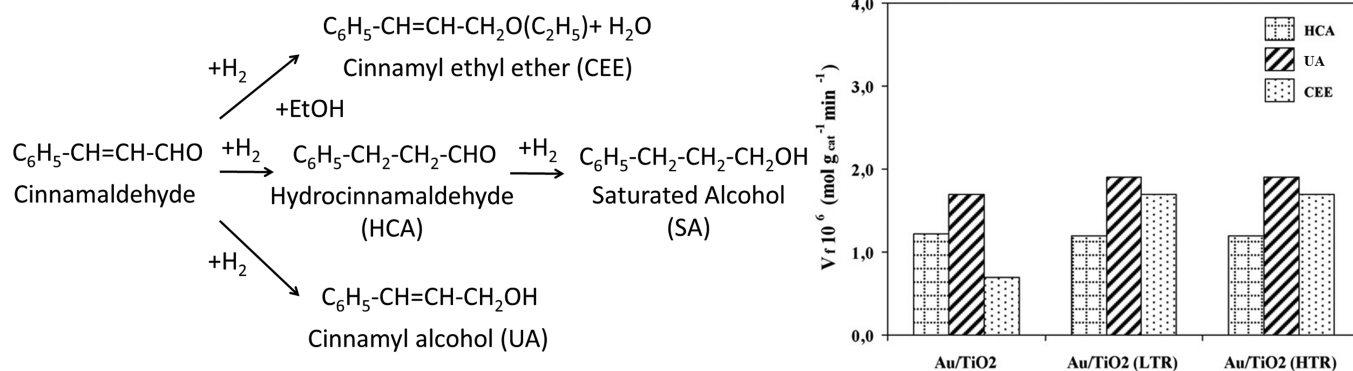
FIGURE 8. Cinnamaldehyde hydrogenation on classical Au/TiO$_2$ catalsyts.[46] Reproduced with permission. Copyright 2012 Elsevier.

TABLE 1. Comparison of Oxidation and Hydrogenation Chemistry of Au(111)

Modified model gold surfaces		O/Au(111)	H/Au(111)
Adsorbate source		Atomic oxygen	Atomic hydrogen
Desorption temperature		~ 500 K	~ 110 K
Reactions with alcohol or aldehyde	Channel 1	Selective oxidation: alcohol → aldehyde	Selective hydrogenation: aldehyde → alcohol
	Channel 2	Oxidative coupling: alcohol + O → ester	Reductive coupling: aldehyde + H → ether
		alcohol + aldehyde + O → ester	aldehyde + alcohol + H → ether
Substantial reaction intermediate			

catalysts as received from the World Gold Council, reduced in H$_2$ at 473 K and reduced at 773 K, respectively. The results indicate that the reduced catalysts yield higher selectivity toward ethers.[46]

5. Concluding Remarks

To sum up, model gold surfaces are active for both selective oxidation and hydrogenation reactions. In particular, oxygen-modified Au(111) induces alcohol oxidation to aldehyde and further facilitates a coupling reaction between alcohols and aldehydes to generate esters. In contrast, hydrogen covered Au(111) mediates aldehyde hydrogenation to produce alcohols and also results in the coupling reaction of aldehyde—aldehyde or aldehyde—alcohol for ether production. These two reactions have also been observed from high-surface-area gold catalysts.

Table 1 illustrates the comparison of alcohol oxidation and aldehyde hydrogenation on Au(111). For both

molecular oxygen and hydrogen, Au(111) has a high barrier for dissociation. Therefore, atomic oxygen and hydrogen have been employed to populate the surface. These weakly chemisorbed oxygen and hydrogen atoms result in the unique surface chemistry of gold, which induce selective oxidation and hydrogenation reactions. Oxygen and hydrogen modified Au(111) surfaces act as H acceptor and donor catalysts, respectively. These surfaces lead adsorbed alcohols and aldehydes to form different surface intermediates, such as alkoxy groups and alcohol-like compounds, respectively. Au(111) can also induce a coupling reaction on both modified surfaces. However, these surface intermediates cause different reaction pathways, resulting in the production of esters on O/Au(111) and ethers on H/Au(111). These studies elucidate gold catalytic activity from a mechanistic viewpoint and demonstrate that gold is a versatile catalyst with a wide range of potential applications.

BIOGRAPHICAL INFORMATION

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FOOTNOTES

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