

## Surface Science Investigations of Oxidative Chemistry on Gold

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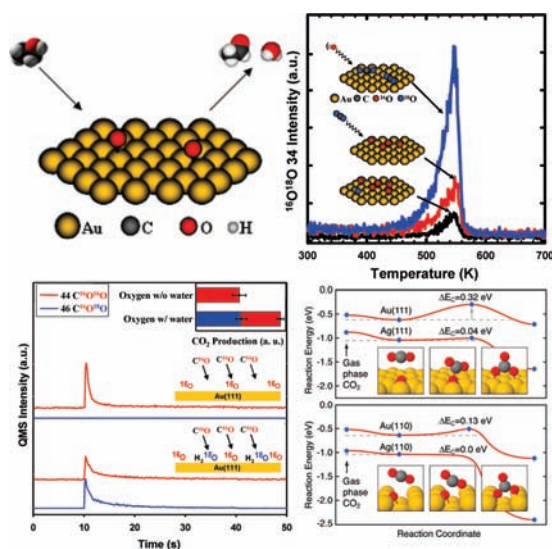
### CON SPECTUS

Because of gold's resistance to oxidation and corrosion, historically chemists have considered this metal inert. However, decades ago, researchers discovered that highly dispersed gold particles on metal oxides are highly chemically active, particularly in low-temperature CO oxidations. These seminal findings spurred considerable interest in investigations and applications of gold-based materials. Since the discovery of gold's chemical activity at the nanoscale, researchers found that bulk gold also has interesting catalytic properties. Thus, it is important to understand and contrast the intrinsic chemical properties of bulk gold with those of nanoparticle Au.

Despite numerous studies, the structure and active site of supported Au nanoclusters and the active oxygen species remain elusive, and model studies under well-controlled conditions could help identify these species. The {111} facet has the lowest surface energy and is the most stable and prevalent configuration of most supported gold nanoparticles. Therefore, a molecular-level understanding of the physical properties and surface chemistry of Au(111) could provide mechanistic details regarding the nature of Au-based catalysts and lead to improved catalytic processes.

This Account focuses on our current understanding of oxidative chemistry on well-defined gold single crystals, predominantly from recent investigations on Au(111) that we have performed using modern surface science techniques. Our model system strategy allows us to control reaction conditions, which assists in the identification of reaction intermediates, the determination of the elementary reaction steps, and the evaluation of reaction energetics for rate-limiting steps.

We have employed temperature-programmed desorption (TPD), molecular beam reactive scattering (MBRS), and Auger electron spectroscopy (AES) to evaluate surface oxidative chemistry. In some cases, we have combined these results with density functional theory (DFT) calculations. By controlling the reaction parameters that determine product selectivity, we have examined the chemical properties of bulk gold. Based on our investigations, the surface-bound oxygen atoms are metastable at low temperature. We also demonstrate that the oxygen atoms and formed hydroxyls are responsible for some of the distinct chemical behavior of gold and participate in surface reactions either as a Brønsted base or a nucleophilic base. We observe similar reaction patterns on gold surfaces to those on copper and silver surfaces, suggesting that the acid–base reactions that have been observed on copper and silver may also occur on gold. Our model chemical studies on gold surfaces have provided intrinsic fundamental insights into high surface area gold-based catalysts and the origin of the reactive oxygen species.



### 1. Introduction

Fascination with gold, Au ( $[Xe]4f^{14}5d^{10}6s^1$ ), has persisted for millennia in part due to its inertness, and thus the chemistry of gold was previously

undeveloped. Recent work regarding Au-based heterogeneous catalysts has been inspired by the discovery of the catalytic activity of highly dispersed gold nanoparticles supported on oxides,<sup>1</sup>

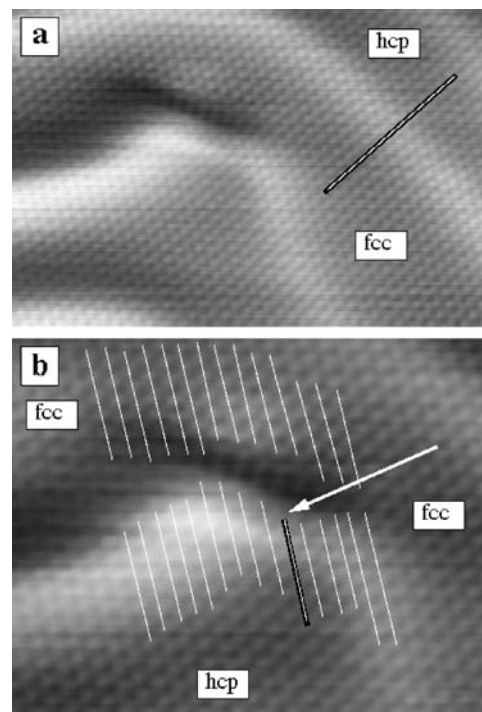
particularly for CO oxidation.<sup>2,3</sup> Indeed, due to fundamental and applied aspects relevant to the support, particle size and shape, and structural sensitivity, these subjects are now more intensively investigated,<sup>2–8</sup> since their effects on reactivity and selectivity remain unclear.<sup>1</sup> This, in turn, renders careful and thorough model studies a necessity.<sup>9–12</sup> Furthermore, due to the relative complexity of Au particles/films supported on planar oxide substrates, studies of gold single crystals under well-controlled conditions may provide useful details regarding Au-based catalysts.

Gold exhibits a high ionization potential (9.2 eV), work function (5.3 eV), and electron affinity (2.3 eV) and is a poor electron donor. Therefore, upon being oxidized by chemical treatment, cationic gold shows high reactivity. This allows atomic oxygen covered Au surfaces to be potential model systems for investigating oxidation chemistry.

Here, we present our recent efforts regarding fundamental investigations of low-temperature oxidative chemistry on gold single crystals. The {111} facet is the most stable and prevalent configuration of supported gold nanoparticles;<sup>1</sup> therefore an understanding of Au(111) surface chemistry could be insightful regarding the chemistry of supported Au nanoparticles. We will discuss several recently studied oxidative reactions that are promoted by gold. First, classical oxidation chemistry on gold surfaces is reviewed, including low-temperature CO oxidation, formation and decomposition of surface carbonate, and oxidation of nitric oxide. Next, the role of oxygen atoms as a Brønsted base or a nucleophilic base<sup>13</sup> is illustrated for oxidative dehydrogenation of water, ammonia, amines, and alcohols. The relationships between the low-pressure surface science studies and more practical catalytic conditions are also discussed. Excellent review articles regarding other aspects of Au catalysis are also available.<sup>1,5,7,9–12,14–16</sup>

## 2. Adsorption of Oxygen on Au(111)

Gold is the only element for which the (111) surface reconstructs under UHV conditions.<sup>1</sup> Au(111) is the lowest energy surface of gold, as reflected in the tendency of thin-film growth to propagate in the [111] direction. The reconstructed surface of Au(111) is characterized by a 4.3% uniaxial lateral contraction relative to the bulk layers. The contraction causes variations in registry between the surface and subsurface atomic layers leading to the alternation of stacking arrangement between normal ABC stacking and faulted ABA stacking with faulted and unfaulted regions delineated by

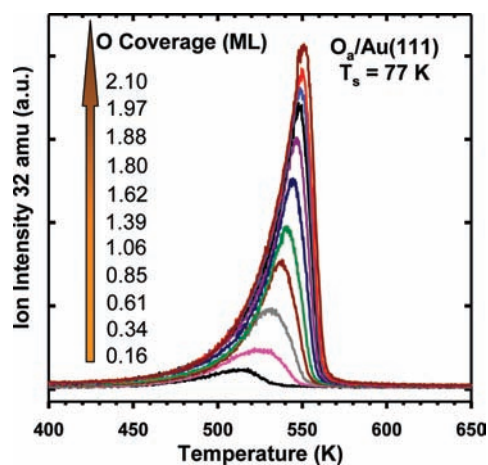


**FIGURE 1.** STM images of clean Au(111) showing a closeup of the bulged herringbone corner: (a)  $11 \times 7 \text{ nm}^2$  image showing the transition between fcc and hcp stacking; (b) a zoomed-in portion of the image in panel a,  $6.6 \times 5.2 \text{ nm}^2$ . The white lines align the atomic rows across the herringbone corner with one extra column appearing in the hcp region indicated by the arrow.<sup>17</sup> Reproduced with permission from ref 17. Copyright 1992 American Institute of Physics.

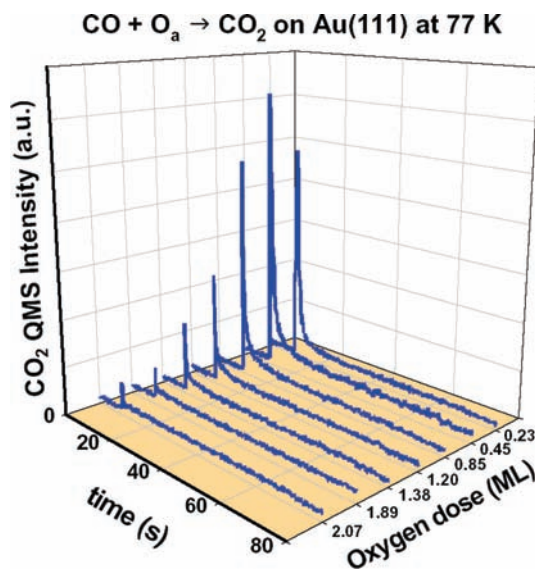
rows of bridging Au atoms (see Figure 1).<sup>17</sup> These bridging rows are manifest in scanning tunneling microscopy (STM) topography as elevated ridges aligned with the substrate  $\langle 121 \rangle$  directions. They pair, forming a  $(\sqrt{3} \times 22)$  surface unit cell that can adopt one of three orientational registries. To further reduce surface energy, the pairs form hyperdomains characterized by alternating  $60^\circ$  bends reminiscent of a herringbone pattern.<sup>18</sup>

There have been many efforts over the years to investigate the nature of oxygen on gold.<sup>2,12,13,19</sup> Gold single-crystal surfaces do not measurably chemisorb oxygen either molecularly or dissociatively under UHV conditions<sup>20</sup> or at elevated temperature and pressure;<sup>1</sup> however molecular oxygen will physically adsorb up to  $\sim 45 \text{ K}$ .

The inability to populate gold surfaces with oxygen via exposure to gaseous molecular oxygen has motivated researchers to develop other means of creating atomic oxygen precovered gold surfaces. Successful approaches include thermal dissociation of gaseous  $\text{O}_2$  on hot filaments, ozone decomposition, coadsorption of  $\text{NO}_2$  and  $\text{H}_2\text{O}$ ,  $\text{O}^+$  sputtering, electron-induced adsorption of oxygen, and electron bombardment of condensed  $\text{NO}_2$ . In the studies discussed here, we



**FIGURE 2.** O<sub>2</sub> TPD spectra on Au(111) (heating rate  $\beta = 3$  K/s). Atomic oxygen was dosed at 77 K using a radio frequency-generated plasma jet.



**FIGURE 3.** CO<sub>2</sub> signal from atomic oxygen precovered Au(111) surfaces at 77 K during CO molecular beam impingement. CO beam starts at 10 s for all oxygen coverages.

chase to populate atomic oxygen onto Au(111) via a supersonic, RF-generated plasma jet<sup>8,21–33</sup> using an 8% (vol.) O<sub>2</sub> in argon mixture with  $\sim 40\%$  dissociation fraction.<sup>8</sup> It is notable that the achievable saturation oxygen coverages are strongly dependent on the preparation methods.

Due to the reconstruction of clean Au(111) to the herringbone structure, upon oxygen adsorption, gold atoms are released from the surface, leading to the formation of oxidized gold (Au–O) nanoclusters on Au(111) and consequently a rough surface morphology.<sup>10</sup> The local bonding characteristics of these oxygen atoms also depend on the coverage and surface temperature, which, as will be discussed later, determines the reactivity and selectivity of oxidative reactions.

Temperature-programmed desorption (TPD) spectroscopy is widely used to obtain information on the nature of adsorbate species as well as adsorption energies and surface structure. Figure 2 shows a series of oxygen TPD spectra with various initial coverages on Au(111). Oxygen coverages were typically determined by comparing the integrated area under the corresponding O<sub>2</sub> TPD spectrum with that of a saturation coverage of  $\sim 2.1$  ML (1 ML is defined as  $1.387 \times 10^{15}$  molecules or atoms cm<sup>-2</sup>).<sup>26</sup> The desorption activation energy of oxygen from Au(111) based on a Redhead analysis is  $\sim 126$  kJ/mol at an atomic oxygen coverage of 0.16 ML, increasing to  $\sim 134$  kcal/mol at 1.0 ML, consistent with values in which oxygen atoms are prepared by other methods.

### 3. Oxidation of Carbon Monoxide on Au Surfaces

The discovery of catalytic activity in the low-temperature oxidation of CO by supported gold nanoparticles (2–5 nm)

helped spur the growth in investigations of heterogeneous gold catalysis.<sup>19</sup> Despite considerable effort, much remains to be learned; the nature of the active species, the mechanism of O<sub>2</sub> activation, and the oxidation state of Au are still controversial.<sup>1</sup> Of particular interest is how effectively gold itself catalyzes oxidation of carbon monoxide.<sup>34</sup> Fortunately, model investigations using gold crystals can provide insight into the intrinsic activity of Au in the absence of a support.<sup>10,26,35–37</sup>

CO oxidation was first examined on Au(110) by Madix's group<sup>36</sup> and later by Christmann's group.<sup>37</sup> Outka et al. oxidized CO on oxygen precovered Au(110) and estimated an apparent activation energy of  $8 \pm 4$  kJ/mol.<sup>36</sup> Gottfried et al. showed that at low oxygen coverages, the reaction on Au(110) is first-order in oxygen coverage with an apparent activation energy of  $-1.8$  kJ/mol.<sup>37</sup> Friend et al.<sup>10</sup> as well as Koel et al.<sup>35</sup> observed CO oxidation on Au(111) populated with atomic oxygen. We have extended their pioneering results to reaction temperatures as low as 77 K and have also investigated the effects of oxygen coverage and annealing temperature and the role of adsorbed water.

CO<sub>2</sub> can be produced efficiently from impinging a CO beam on Au(111) precovered with various O coverages (0.23–2.07 ML) at 77 K<sup>26</sup> (Figure 3) and can be measured via molecular beam reactive scattering (MBRS).<sup>38</sup> The initial adsorption probability of an impinging CO molecule was measured to be  $\sim 1/3$  for an oxygen coverage of 0.45 ML at 77 K and does not vary significantly for other coverages.<sup>26</sup> For all oxygen coverages, prompt CO<sub>2</sub> production was observed followed by a sharp decrease due to the accumulation of CO on the surface at 77 K. Additionally, there is a strong oxygen coverage

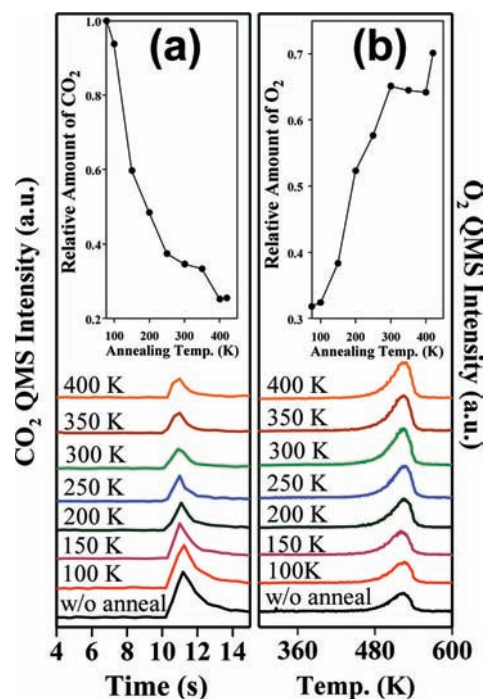


dependence at 77 K. For oxygen coverages up to 0.5 ML, CO<sub>2</sub> production increases with higher oxygen coverage due to the additional availability of oxygen. At oxygen coverages above 0.5 ML, the initial CO<sub>2</sub> production decreases with increasing oxygen coverage; likely due to the change in the nature of the adsorbed oxygen atoms and structural and electronic properties of the Au(111) surface as a function of oxygen coverage as suggested by Min and Friend<sup>10</sup> (and not a reduction in CO adsorption<sup>26</sup>). It has been shown that the adsorption of 1.0 ML of oxygen atoms on Au(111) increases the work function by +0.80 eV, indicating electron transfer from the Au substrate into the oxygen adlayer (i.e., the oxygen-induced formation of Au<sup>δ+</sup> sites). The order of reactivity of atomic oxygen has been classified by Friend and co-workers as follows: chemisorbed (metastable) oxygen > oxygen in a surface oxide (i.e., well-ordered 2D Au–O phase) > oxygen in a bulk gold oxide (i.e., 3D structures containing Au and O).<sup>10</sup> It appears that oxide-like domains may exist only at the higher coverage, while chemisorbed oxygen on Au(111) plays a more dominant role at the lower coverages.

**Effect of Annealing the O<sub>a</sub> Overlayer.** It is believed that oxygen adsorbed at low temperatures (i.e., 77 K) is trapped in a metastable state from which the barrier to further reaction is lowered. Annealing the adsorbed oxygen may stabilize the oxygen overlayer, thereby increasing the barrier to reaction. Indeed, annealing-induced oxygen stabilization also applies to CO oxidation reactions (see Figure 4). Specifically, CO<sub>2</sub> production decreases with increasing annealing temperature, with the highest CO<sub>2</sub> production occurring with no annealing, consistent with increases in the amount of unreacted oxygen with increasing annealing temperature [Figure 4b]. These results support a change from chemisorbed to bulk oxide upon annealing O–Au(111) from 77 to 400 K.<sup>10</sup> That is, metastable and disordered Au–O phases may play a role in determining or enhancing chemical reactivity, particularly in low-temperature processes.

#### 4. Formation of Carbonate from CO<sub>2</sub> and Adsorbed Atomic Oxygen

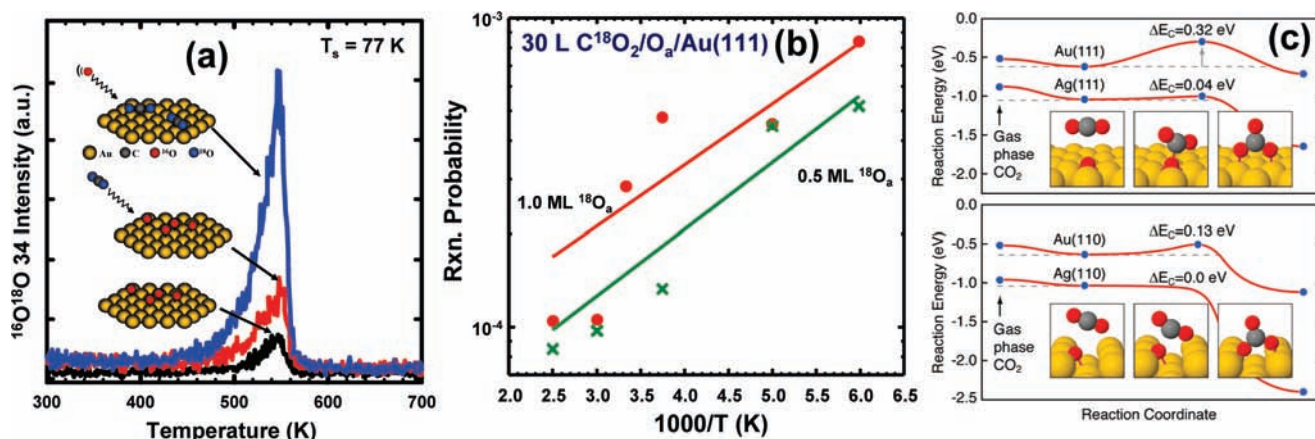
The carbonate formation and decomposition (CO<sub>3</sub> ↔ CO<sub>2</sub> + O<sub>a</sub>) reaction on gold is important regarding low-temperature CO oxidation since it has been proposed as a possible reaction intermediate.<sup>39</sup> A surface carbonate is readily formed in UHV on silver when oxygen-precovered Ag(110) is exposed to CO<sub>2</sub> at 300 K.<sup>40</sup> Despite similarities between silver and gold, carbonate formation and decomposition went undetected pre-



**FIGURE 4.** (a) CO<sub>2</sub> evolution at 77 K from 0.37 ML <sup>16</sup>O covered Au(111) surfaces annealed at varying temperatures at  $\beta = 1$  K/s and cooled to 77 K in each case before 10 s CO dose. (b) TPD spectra showing unreacted O<sub>2</sub> remaining on the Au(111) surface after reaction in each of the above cases. The lowest curves represent (a) CO<sub>2</sub> evolution from an unannealed surface and (b) TPD of the remaining oxygen on the unannealed surface. The insets show the normalized amount of (a) CO<sub>2</sub> produced and (b) unreacted oxygen as a function of annealing temperature.

viously on Au(110)<sup>36</sup> and Au(111)<sup>35</sup> likely due to its low reaction probability.

In our investigations, the surface carbonate on gold was detected via a reaction of preadsorbed <sup>16</sup>O atoms and gaseous C<sup>18</sup>O<sub>2</sub>, which decomposes to form either C<sup>18</sup>O<sub>2</sub> or C<sup>18</sup>O<sup>16</sup>O while leaving either <sup>16</sup>O<sub>a</sub> or <sup>18</sup>O<sub>a</sub> adatoms on the surface, respectively.<sup>28</sup> Upon heating, the oxygen atoms recombinatively desorb to form <sup>16</sup>O<sub>2</sub> and <sup>16</sup>O<sup>18</sup>O (and negligible <sup>18</sup>O<sub>2</sub>). Therefore, carbonate formation and decomposition can be measured by monitoring the presence of mass 34 (<sup>18</sup>O<sup>16</sup>O) in the TPD spectra. An increase in <sup>16</sup>O<sup>18</sup>O desorption is observed from C<sup>18</sup>O<sub>2</sub> and <sup>16</sup>O coadsorbed on Au(111) compared with the solely <sup>16</sup>O covered surface [black and red curves in Figure 5a]. An Arrhenius plot of the reaction probability ( $\sim 10^{-3}$ – $10^{-4}$ ) for two oxygen coverages (0.5 and 1.0 ML) yields similar apparent activation energies of  $E_a = -0.15 \pm 0.08$  eV [Figure 5b], suggesting a competition between carbonate formation and CO<sub>2</sub> desorption on the O/Au(111) surface.<sup>28</sup> Compared with Au(111), the carbonate formation reaction on Ag(110) is very facile.<sup>40</sup> This difference could be related to surface structure and energetics. Density functional



**FIGURE 5.** (a) TPD spectra of  $^{16}\text{O}^{18}\text{O}$  after (black curve) dosing 1.3 ML of  $^{16}\text{O}$  on clean Au(111); (red curve) back-filling 30 L of  $\text{C}^{18}\text{O}_2$  on Au(111) precovered with 1.3 ML of  $^{16}\text{O}$ ; (blue curve) dosing 1.3 ML of  $^{16}\text{O}$  on Au(111) precovered with 30 L of  $\text{C}^{18}\text{O}_2$  via back-filling.<sup>30</sup> All exposures are at 77 K, and the heating ramps are 3 K/s. (b) Arrhenius plot of  $\text{C}^{18}\text{O}_2$  reaction probability using a constant  $\text{C}^{18}\text{O}_2$  exposure of 30 L for 1.0 ML (red circles with red linear fit) and 0.5 ML (green crosses with green linear fit) of atomic oxygen on Au(111).<sup>28</sup> (c) DFT calculations of carbonate formation on Au and Ag (111) and (110) surfaces. Energy barriers ( $\Delta E_c$ ) are labeled for each reaction pathway.<sup>28</sup> Reproduced with permission from refs 28 and 30. Copyright 2008 American Chemical Society.

theory (DFT) calculations provide the difference in energetics and reaction paths for  $\text{CO}_3$  formation on Au(111), Au(110), Ag(111), and Ag(110) [Figure 5c]. The formation of  $\text{CO}_3$  on Ag(110) was found to be spontaneous and occurs with only a very small barrier ( $\sim 0.04$  eV) on Ag(111). For Au, however, there is a significant barrier to  $\text{CO}_3$  formation [particularly on the (111) surface] and  $\text{CO}_3$  is bound much more strongly to Ag, consistent with the experimental results.

Changing the order of deposition of  $\text{CO}_2$  and O leads to different reaction phenomena and mechanisms. By direction of an  $^{16}\text{O}$  atomic beam toward  $\text{C}^{18}\text{O}_2$  preadsorbed Au(111) [blue curve in Figure 5a], the formed carbonate increases significantly (by a factor of  $\sim 4$ ) compared with exposing  $\text{C}^{18}\text{O}_2$  to the  $^{16}\text{O}_a$  precovered Au(111) surface, indicating that the nature of the adsorbed atomic oxygen (i.e., excited or ground state) plays a significant role in carbonate formation reactions. Such a reaction could follow a hot-precursor-mediated mechanism.<sup>30</sup> These results may provide insight into the related reaction between CO and adsorbed molecular oxygen  $\text{O}_{2,a}$  to make  $\text{CO}_2$ , in which a “hot” oxygen adatom is produced that could encounter other adsorbed moieties and react further.

## 5. Oxidation of Nitric Oxide on Au(111)

Nitrogen oxides exhibit interesting chemistry on bulk gold surfaces. In addition to catalytic reduction of  $\text{NO}_x$ , selective oxidation of NO is significant from the practical point of view. We have shown that NO uptake on the Au(111) surface is enhanced by the presence of oxygen adatoms, likely due to electronic or structural changes in the Au surface.<sup>23</sup> At temperatures above 200 K,  $\text{NO}_2$  production

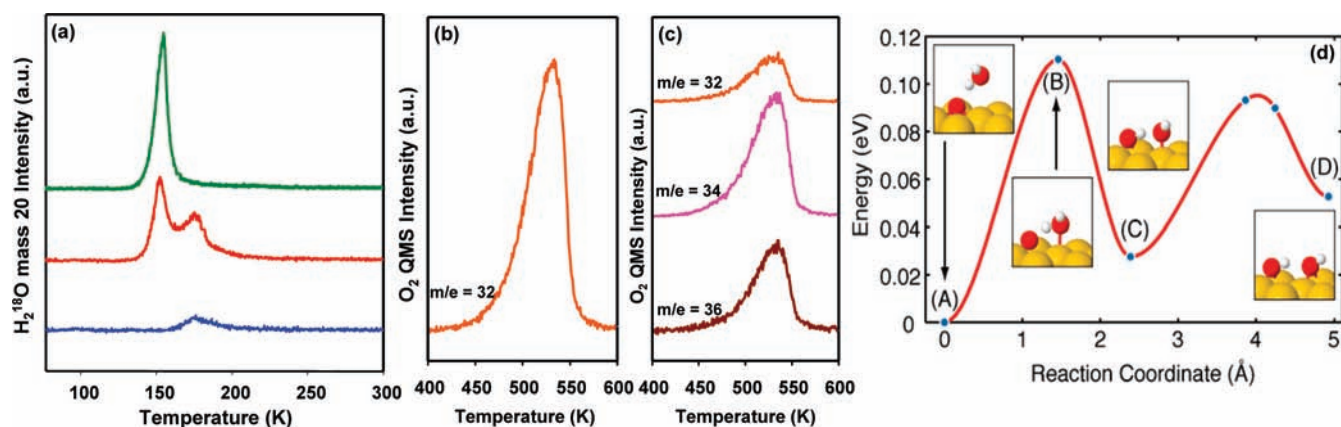
becomes limited by the surface lifetime of the adsorbed NO species. Below 200 K, nitric oxide can react with surface oxygen to form a chemisorbed  $\text{NO}_2$  product. Based on an analysis involving a kinetic competition between desorption of the NO molecule and reaction with O adatoms, an activation energy ( $E_r = 0.21 \pm 0.02$  eV) is estimated for the 0.95 ML O/Au(111) surface.<sup>23</sup>

## 6. Interaction of Water and Oxygen Atoms and Its Role in CO Oxidation on Au(111)

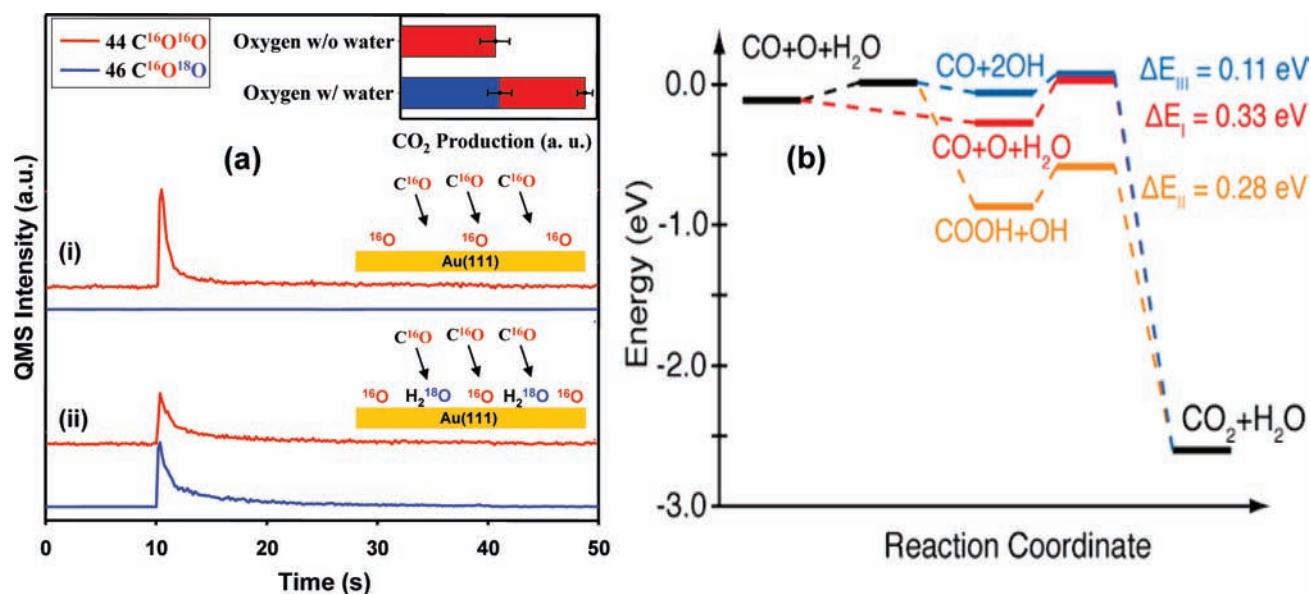
On Au(111), water strongly interacts with oxygen atoms to make a water–oxygen complex or hydroxyls<sup>24,26,27,35,41</sup> as evidenced by a new TPD feature with its peak near 175 K, in addition to the water desorption feature at 155 K characteristic of the clean Au(111) surface [see Figure 6a]. Water–oxygen interactions also produce oxygen scrambling on Au(111) as evidenced from isotopic mixing in the oxygen evolution in TPD measurements [Figure 6b,c]. Oxygen atoms from adsorbed water exchange with adsorbed oxygen adatoms on Au(111) due to rapid diffusion of transient OH groups with subsequent reversible reactions between two nearby adsorbed hydroxyl groups to adsorbed water and oxygen. DFT calculations also show that hydroxyls are readily formed by water on oxygen precovered Au(111) due to the small calculated activation barrier of 0.11 eV [Figure 6d]. A recent investigation by Quiller et al. suggests that isolated *stable* hydroxyls may not be formed and could be more transient in character.<sup>41</sup>

Water plays an important role in many oxidation reactions and has been a subject of recent research efforts on





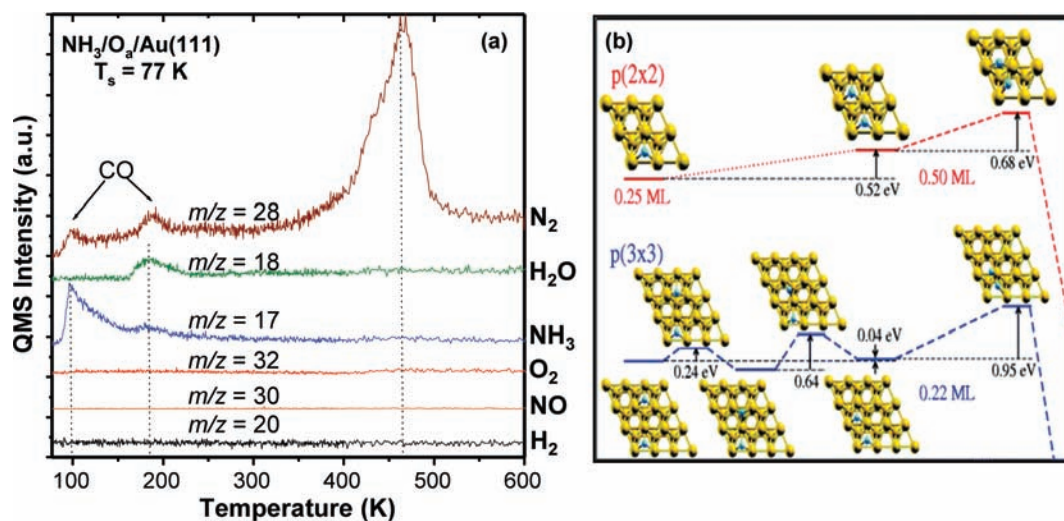
**FIGURE 6.** (a) TPD ( $\beta = 1$  K/s) of 0.6 ML of  $\text{H}_2^{18}\text{O}$  on a clean Au(111) surface (green curve), 0.6 ML of  $\text{H}_2^{18}\text{O}$  on 0.18 ML of  $^{16}\text{O}$  covered surface (red curve) and 0.1 ML of  $\text{H}_2^{18}\text{O}$  on 0.18 ML of  $^{16}\text{O}$  covered surface (green curve). TPD ( $\beta = 3$  K/s) of oxygen after dosing (b) 0.37 ML of  $^{16}\text{O}$  and (c) 0.6 ML of  $\text{H}_2^{18}\text{O}$  in addition to 0.37 ML of  $^{16}\text{O}$  on Au(111) surface. All exposures at 77 K. (d) The reaction paths of formation of hydroxyls from water and atomic oxygen with a barrier of 0.11 eV.<sup>27</sup> Reproduced with permission from ref 27. Copyright 2008 American Chemical Society.



**FIGURE 7.** (a) Evolution of  $\text{CO}_2$  at 140 K while impinging a continuous CO beam (10–40s) at the surface. Red curve represents mass 44  $\text{C}^{16}\text{O}^{16}\text{O}$  and blue curve represents mass 46  $\text{C}^{16}\text{O}^{18}\text{O}$  with (i) 0.08 ML of  $^{16}\text{O}$  preadsorbed or (ii) 0.1 ML  $\text{H}_2^{18}\text{O}$  in addition to 0.08 ML of  $^{16}\text{O}$  atoms preadsorbed on Au(111) at 77 K.<sup>24</sup> (b) Energy landscape for three reaction mechanisms of CO oxidation in the presence of  $\text{H}_2\text{O}$ . In pathway I (red), there is no hydrogen transfer from  $\text{H}_2\text{O}$ . In pathway II (orange), hydrogen transfer occurs before CO oxidation. In pathway III (blue), hydrogen transfer occurs concertedly with CO oxidation, leading to the lowest overall barrier for CO oxidation (0.11 eV).<sup>27</sup> Reproduced with permission from refs 24 and 27. Copyright 2006 and 2008 American Chemical Society.

gold. Daté and Haruta showed that the addition of water in the feed stream enhances the CO oxidation reaction over supported gold particles by as much as 2 orders of magnitude.<sup>39</sup> They postulated that water promotes the reaction by either activating molecular oxygen on the surface or assisting in the decomposition of carbonates that may accumulate on the surface in order to accommodate additional reactants on the surface. However, our results suggest direct involvement of water in the reaction as shown from the evolution of  $\text{C}^{16}\text{O}^{18}\text{O}$  after  $\text{C}^{16}\text{O}$  impingement on Au(111) covered with both oxygen ( $^{16}\text{O}_a$ ) and isotopically labeled

water ( $\text{H}_2^{18}\text{O}$ ) [Figure 7a]. For example, with 0.08 ML of  $^{16}\text{O}$  preadsorbed on the surface,  $\sim 70\%$  more  $\text{CO}_2$  production is observed at 140 K with added water (0.1 ML).<sup>24,27</sup> DFT calculations indicate that in the presence of  $\text{H}_2\text{O}$ , the barrier for CO oxidation for a select pathway is reduced to 0.11 eV [see Figure 7b] compared with 0.25 eV for CO oxidation on oxygen precovered Au(111) without  $\text{H}_2\text{O}$ .<sup>27</sup> This reduction is attributed to a concerted hydrogen transfer from one hydroxyl to another that acts to stabilize the transition state for CO oxidation and reaction at temperatures as low as 45 K.



**FIGURE 8.** (a) TPD spectra for  $\text{H}_2$ ,  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$  from the adsorption of 0.18 ML of O atoms on Au(111) at 77 K followed by 0.23 ML of  $\text{NH}_3$  at 77 K. The sample was heated with a rate of 1 K/s to 400 K, then 3 K/s to 600 K.<sup>25</sup> (b) N–N recombination energy plots at two different coverages:  $p(2 \times 2)$  and  $p(3 \times 3)$ . Yellow and blue spheres represent Au and N atoms, respectively. Relevant energies are shown in eV.<sup>42</sup> Reproduced with permission from refs 25 and 42. Copyright 2006 and 2008 American Chemical Society.

## 7. Selective Oxidation of Ammonia and Amines on Au(111)

Selective catalytic oxidation of ammonia to nitrogen and water is potentially an ideal technology for removing ammonia from oxygen-containing waste gases, thus selectively avoiding the conversion of nitrogen into its oxides.<sup>25</sup> Pt and Ir are the most active catalysts for  $\text{NH}_3$  oxidation, but they produce significant amounts of nitrogen oxides.<sup>25</sup> However, the selectivity of the catalytic oxidation of ammonia to  $\text{N}_2$  or  $\text{NO}$  on Au(111) is tunable by the amount of surface-bound oxygen.  $\text{N}_2$  recombination is hindered by a barrier of 0.95 eV whereas that of  $\text{NO}$  is 1.03 eV.<sup>25,42</sup> For Au(111) with low oxygen coverages, ammonia can be selectively decomposed to form water and  $\text{N}_2$  without any trace of nitrogen oxides [see Figure 8]. Abstraction of hydrogen from ammonia via the high basic character of O atoms is the initial step in the surface decomposition of  $\text{NH}_3$ . The formed hydroxyl is also a stripping agent for  $\text{NH}_x$  dehydrogenation.<sup>42</sup> Atomic oxygen or hydroxyl-assisted dehydrogenation steps have lower barriers than recombination reactions.

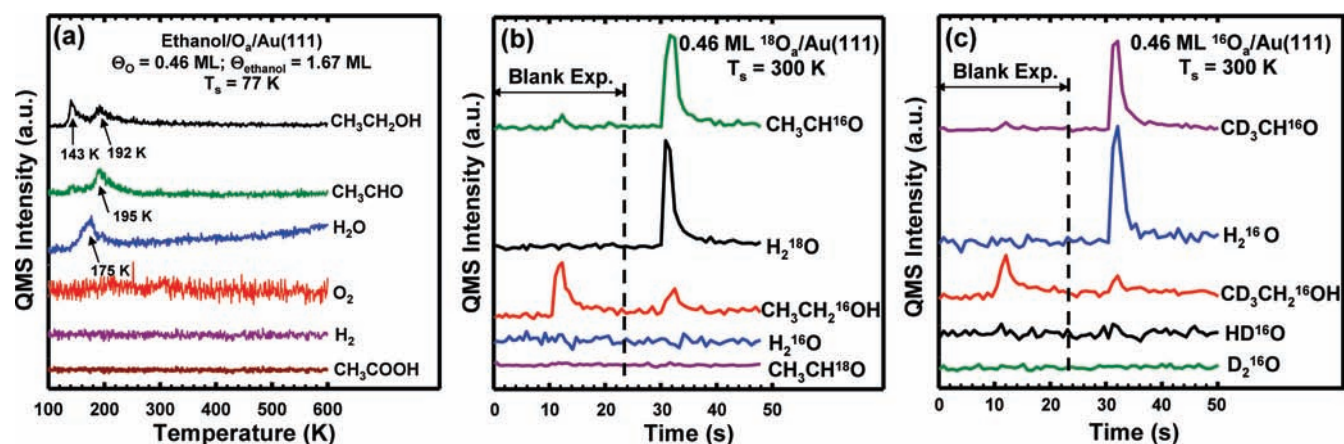
As derivatives of ammonia, amines have been investigated extensively due to their importance in many heterogeneously catalyzed processes. We have recently found that propylamine ( $n\text{-C}_3\text{H}_7\text{NH}_2$ ) can be selectively oxidized to the associated nitrile and aldehyde dependent on oxygen coverage.<sup>33</sup> At low oxygen coverage (i.e.,  $\theta_0 < 0.5$  ML) propylamine initially undergoes N–H bond breaking to produce propionitrile and water, while the formation of propionitrile, propaldehyde, water, CO,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  was observed at higher oxygen coverages.

## 8. Alcohol Oxidation on Au(111)

The selective oxidation of alcohols into aldehydes or ketones is an important step in the synthesis of fine chemicals.<sup>43</sup> For this reason, alcohols have been intensively investigated in both model and practical catalytic systems. For clean single-crystal coinage metals, alkyl alcohols adsorb at cryogenic temperatures without dissociation, and during heating there is no evidence for decomposition. However, it is well-known that the Brønsted-base character of oxygen adatoms on the group 1B metals induces the abstraction of acidic hydrogen from different adsorbates.<sup>13,44</sup> This makes atomic oxygen precovered Au crystals well-defined model systems for investigating the surface chemistry of alcohols.

**Methanol.** Oxidation of  $\text{CH}_3\text{OH}$  has been investigated on both Au(110)<sup>13</sup> and Au(111).<sup>29,35,45</sup> Outka and Madix showed that abstraction of the hydrogen atom bound to the oxygen in methanol is the initial reaction step on oxygen covered Au(110) to form surface-bound methoxy [ $\text{CH}_3\text{O}_{(a)}$ ] and hydroxyl.<sup>13</sup> Methoxy decomposes to form surface formaldehyde, which further reacts with methoxy or oxygen adatoms/hydroxyls to form methyl formate or formate groups. Methyl formate desorbs from Au(110) at  $\sim 270$  K, while the formate decomposes to  $\text{CO}_2$ , which desorbs at  $\sim 340$  K.<sup>13</sup> Similar surface reactions occur on O–Au(111) regarding the formation of methoxy intermediate,<sup>29,45</sup> which, at low oxygen coverages, further reacts forming methyl formate when atomic oxygen (via ozone decomposition) and methanol were exposed at 200 and 160 K, respectively.<sup>45</sup> However, if the surface is coadsorbed with atomic oxygen (via O-plasma) and metha-





**FIGURE 9.** (a) TPD spectra ( $\beta = 1$  K/s) following adsorption of 1.67 ML ethanol on atomic oxygen precovered Au(111) at 77 K. Evolution of acetaldehyde and water from (b)  $\text{C}_2\text{H}_5\text{OH}$  impingement on  $^{18}\text{O}_a$  precovered Au(111) at 300 K and (c)  $\text{CD}_3\text{CH}_2\text{OH}$  impingement on  $^{16}\text{O}_a$  precovered Au(111) at 300 K. A blank experiment is shown at  $t \approx 10$ – $12$  s where an ethanol beam is impinged on an inert-stainless-steel flag placed in front of Au(111). The sample is heated to 300 K prior to impinging a continuous ethanol beam ( $t = 30$ – $32$  s) on the surface. Atomic oxygen is deposited on Au(111) at 77 K with a coverage of  $\sim 0.46$  ML.<sup>31</sup> Reproduced with permission from ref 31. Copyright 2008 American Chemical Society.

nol at 77 K, methoxy only decomposes to produce  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{CO}_2$ , while no other partial oxidation products or derivatives such as formaldehyde, formic acid, or methyl formate can be detected.<sup>29,45</sup> This difference indicates that the preparation method of atomic oxygen and the surface temperature in which reactants were adsorbed play a crucial role in determining the reaction pathway.

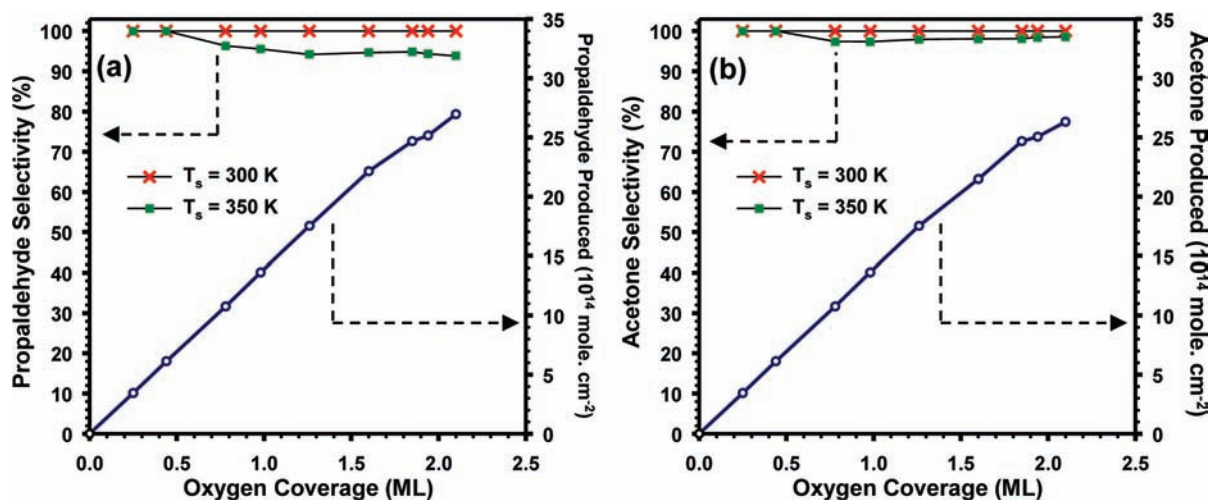
**Ethanol.** Interestingly, unlike methanol chemistry on  $\text{O}-\text{Au}(111)$ , ethanol is *selectively* oxidized on Au(111) as indicated by the formation of acetaldehyde (and water) [Figure 9a] for low oxygen coverages. No other partial oxidation products, such as methane, ethane, ethylene, ethenol, acetic acid, ethylene oxide, methyl formate, and ethyl acetate, as well as  $\text{C}_1$ -containing species (e.g.,  $\text{CO}$ ,  $\text{CO}_2$ , formaldehyde, and formic acid) were detected during the reaction.<sup>31</sup> Ethanol initially undergoes  $\text{O}-\text{H}$  bond cleavage (producing ethoxide) followed by selective  $\beta\text{-C}-\text{H}$  bond ( $\alpha$  to the oxygen) elimination to form acetaldehyde and water on atomic oxygen precovered Au(111). Isotopic experiments provide evidence of the absence of cleavage of the  $\text{C}-\text{O}$  [Figure 9b] and the  $\gamma\text{-C}-\text{H}$  bonds [Figure 9c].<sup>31</sup> At higher oxygen coverages (i.e., 1.0 ML), in addition to acetaldehyde and water,  $\text{CO}_2$  was also formed during the reaction due to the cleavage of the  $\gamma\text{-C}-\text{H}$  bond and the  $\text{C}-\text{C}$  bond. Interestingly, Madix et al. showed that ethanol could be oxidized to ethyl acetate and acetic acid on Au(111) precovered with 0.4 ML atomic oxygen, when prepared by decomposition of  $\text{O}_3$  at 200 K.<sup>44</sup>

**Propanol.** Similar to the surface oxidation chemistry of ethanol, both 1-propanol and 2-propanol can be oxidized to propaldehyde and acetone on oxygen precovered Au(111), respectively.<sup>32</sup> Remarkably, the reactions are 100% selective

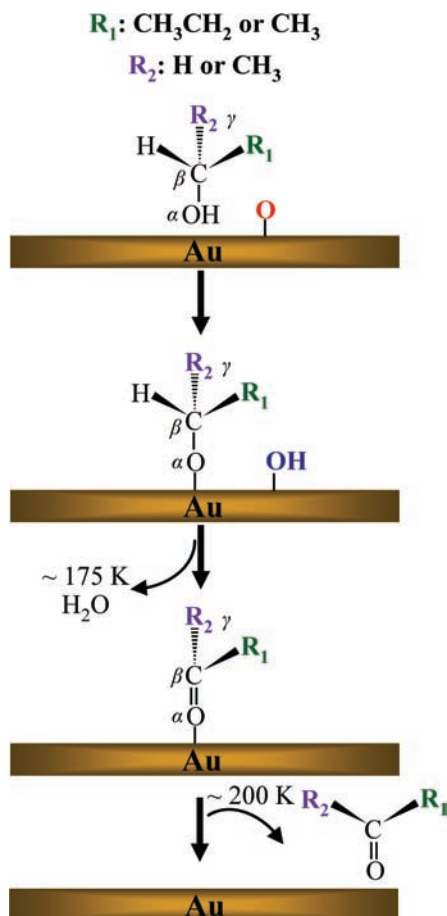
to propaldehyde or acetone at low surface temperatures (i.e., 300–325 K) for all oxygen precoverages investigated [see Figure 10]. For high oxygen precoverages (i.e., above 0.5 ML) and surface temperatures (350–400 K), a small amount of  $\text{CO}_2$  (less than 5%) was formed. The amount of propaldehyde or acetone produced during transient scattering experiments at 300 K is shown in Figure 10 as a function of oxygen coverage. The propanol reaction probability is between 30% and 80% for the various conditions employed. Based on our measurements as well as mechanistic studies on other surfaces,<sup>46</sup> a general reaction scheme for selective oxidation of alcohols to aldehydes or ketones appears in Figure 11.

The results of surface chemistry on model systems provide some mechanistic details for the same reaction on high-surface-area catalysts. However, a particularly ambiguous aspect of the reactions on high-surface-area catalysts is the manner in which molecular oxygen is activated. The first possible mechanism for  $\text{O}_2$  activation involves the formation of an adsorbed hydroperoxy ( $\text{HO}_2$ ).<sup>15</sup> Indeed, hydroperoxy is considered a precursor to the formation of atomically adsorbed oxygen and hydroxyl in the case of coadsorbed water and  $\text{O}_2$  on Au/ $\text{TiO}_2$ .<sup>32</sup> Mechanisms of producing atomic oxygen involving adsorbed water may be especially applicable to processes in which air is used as the oxidant. The second genre of mechanisms for the activation of molecular oxygen on gold catalysts involves those in which water is not present. Oxygen atoms can be created from dissociation of  $\text{O}_2$  at oxygen vacancies on metal oxide surfaces,<sup>47</sup> spillover from Pd to the gold on Pd–Au bimetallic particles, or morphologically rough Au surfaces.<sup>32</sup> These processes are relevant in the case of oxidation of alcohols on Au/ $\text{CeO}_2$ <sup>48</sup> and Pd–Au/ $\text{TiO}_2$ <sup>15</sup> using





**FIGURE 10.** Propaldehyde (a) and acetone (b) production and selectivity as a function of oxygen coverage. Solid symbols represent selectivity to propaldehyde or acetone at 300 (red crosses) and 350 K (green squares), and open symbols indicate overall amount of propaldehyde or acetone produced during reactive scattering measurement (at 300 K). Reproduced with permission from ref 32. Copyright 2008 Wiley-VCH.



**FIGURE 11.** Reaction scheme for selective oxidation of alcohols to aldehydes or ketones on atomic oxygen covered Au.

pure molecular oxygen. In both cases, the oxygen adatoms formed are mobile and can diffuse onto gold to react with alcohols producing aldehydes or ketones via  $\beta$ -hydride elimination.

## 9. Concluding Remarks

Gold-based heterogeneous catalysis has been explored via a considerably increased number of experimental and theoretical investigations including both nanosized gold clusters and gold single crystals. However, mechanistic aspects regarding the activity of supported gold nanoclusters are still debated, especially, the active site structure, particle size dependence, and molecular oxygen activation process. Recent investigations demonstrate that bulk gold precovered by atomic oxygen is very active for low-temperature oxidation of  $\text{CO}$ ,<sup>10,26,35–37</sup> oxidation of ammonia,<sup>25</sup>  $\text{NO}$ ,<sup>23</sup> amines,<sup>33</sup> and alcohols,<sup>13,29,31,32,44,45</sup> and epoxidation of olefins.<sup>10,49</sup> The presence of oxygen atoms is crucial because they act as a Brønsted base or a nucleophilic base.<sup>13</sup> Our investigations demonstrate the intrinsic activity of gold with an activated oxygen species (i.e., atomic oxygen) in the absence of a support, which show the same general patterns of reactivity and selectivity as observed on high surface area Au-based catalysts. Additionally, similar reaction trends on coinage surfaces suggest that the acid–base reactions observed on silver and copper may also occur on gold.<sup>16,46</sup>

The activation of molecular oxygen on gold-based materials is obviously an important concern. There is no general consensus regarding the identity of active oxygen species for high-surface-area gold-based catalysts; the most frequently suggested adsorbed species include atomic oxygen, hydroperoxy ( $^*\text{HO}_2$ ) intermediate, and activated molecular oxygen. Detailed mechanistic studies aimed at understanding the identity of the activated oxygen species are urgently required. Our surface science investigations employing atomic oxygen are

one example and could illustrate elementary reaction steps on “real” gold catalysts. Further model catalytic studies of oxidative reactions over gold single-crystal supported inverse metal oxide [i.e.,  $\text{TiO}_2/\text{Au}(111)$  and  $\text{CeO}_2/\text{Au}(111)$ ] as well as size-selected Au clusters on metal oxide may help elucidate these mechanistic details and design a more efficient gold catalyst for commercial application.

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#### FOOTNOTES

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