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Oxygen Exchange in the Selective Oxidation of 2-Butanol on Oxygen Precovered Au(111)

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Abstract: Direct evidence for C−O bond cleavage in the partial oxidation of 2-butanol on oxygen precovered Au(111) is provided using temperature programmed desorption (TPD) and molecular beam reactive scattering (MBRS) under ultrahigh vacuum (UHV) conditions. The oxygen precovered Au(111) surface can promote the partial oxidation of 2-butanol into 2-butanone with near 100% selectivity at low oxygen coverages, while 2-butanol adsorbs and desorbs molecularly on the clean Au(111) surface. Both $C_2H_5C^{16}OCH_3$ and $C_2H_5C^{18}OCH_3$ are observed in TPD after 2-butanol ($C_2H_5CH^{16}OHCH_3$) was dosed onto Au(111) precovered with $^{18}O_a$. This oxygen exchange phenomenon serves as strong evidence for the C−O bond cleavage in 2-butanol partial oxidation to 2-butanone. Two surface intermediates are proposed for the selective oxidation of 2-butanol: 2-butoxide and η^2-aldehyde. As oxygen coverage increases, full oxidation is activated in addition to selective partial oxidation.

Introduction

In recent years, gold nanoparticles have attracted attention as promising heterogeneous catalysts, because of their high activity in the challenging selective oxidation of alcohols[1−3] and other conversions.[4−9] Abad et al. reported that gold nanoparticles supported by cerium oxide catalyze the selective oxidation of primary and secondary alcohols with high turnover frequencies (TOFs) and selectivities.[2] Enache et al. observed that the addition of Au to Pd nanoparticles improved the selectivity in the partial oxidation of primary alcohols.[3] Biella and Rossi not only showed the high selectivity of Au/SiO_2 for a variety of alcohols but also suggested that relatively large gold clusters (i.e., 15 to 25 nm) play a dominant role in the catalytic process.[1] However, less is known regarding the fundamental aspects of the chemistry.[10] With the hope of better understanding the mechanism, the partial oxidation of alcohols has been studied under ultrahigh vacuum (UHV) conditions using the Au(111) single crystal as a planar representative of supported gold catalysts.[11,12] Herein we report new evidence of oxygen exchange in the selective oxidation of 2-butanol into 2-butanone on oxygen precovered Au(111).

The oxidation reactions of a series of simple alcohols have been studied on Au(111). Previous research showed that methanol is fully oxidized to CO_2, CO, and H_2O on the Au(111) surface exposed to atomic oxygen at a surface temperature of 77 K.[13,14] But ethanol,[15] 1-propanol,[16] and 2-propanol[16] are selectively oxidized to their corresponding aldehydes and ketones with the C−O bonds remaining intact, as revealed by isotope experiments with $^{18}O_a$. Meanwhile, esterification reactions in methanol and ethanol have also been detected on the Au(111) surface oxidized by ozone at 200 K.[17,18] Methanol is converted into methyl formate, formaldehyde, and formic acid via adsorbed methoxy,[17] while ethanol is oxidized to ethyl acetate and acetic acid.[18] These results indicate that the reaction pathways may be influenced by the length of carbon chain and the reaction conditions. More work is required to interpret the versatile and complex reaction pathways in the selective oxidation of alcohols.

In this paper, we present experimental results regarding the partial oxidation of 2-butanol with high selectivity on a Au(111) surface which is precovered with atomic oxygen under UHV conditions. Atomic oxygen covered Au(111) promotes the partial

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oxidation of 2-butanol, leading to the formation of 2-butanone with a small quantity of combustion and dehydration products. Evidence regarding C−O bond cleavage and subsequent oxygen exchange during partial oxidation to 2-butanone is provided via isotope experiments employing $^{18}O_a$. It is our hope that this study will contribute to further understanding of the reaction mechanisms of high-surface-area gold catalysts.

Experimental Section

All the experiments reported here were performed in a molecular beam surface scattering apparatus that has been described in detail elsewhere.[19−21] The apparatus consists of individually pumped vacuum chambers that are divided into two sections: a supersonic molecular beam source section and an ultrahigh vacuum scattering chamber. The supersonic molecular beam source is quadruply differentially pumped to reduce the effusive beam component. Beam defining apertures were recently modified to provide a beam about 6 times larger than that used in previous studies in order to increase measurement sensitivity.[13,15,16,19−21] The molecular beam spot on the sample now has an area of approximately 46 mm^2. The scattering chamber includes the following surface science tools: an Auger electron spectrometer (AES), low-energy electron diffraction optics (LEED), and a quadrupole mass spectrometer (QMS).

The Au(111) crystal used in this study is a thin circular disk with a diameter of ∼11 mm. It is mounted to the sample probe via a tantalum plate and is in thermal contact with a liquid nitrogen reservoir. The Au sample is heated by resistive heating of the tantalum support plate. The sample temperature is measured by a type K thermocouple spot-welded to the Ta plate. An inert flag made of stainless steel can be moved in front of the sample to block the beam from striking the crystal when necessary. The sample was cleaned by cycles of Ar^+ ion bombardment at room temperature and annealing at 850 K, as well as exposure to atomic oxygen at 77 K with subsequent desorption of the oxygen and other oxidation products. The cleanliness of the surface was routinely verified by AES and after each experiment the sample was cleaned by atomic oxygen. Both the molecular beam reactive scattering experiments and temperature programmed desorption (TPD) experiments are conducted in an angle-integrated manner with the sample facing away from the QMS.

Our atomic oxygen beam is generated by a plasma source, which is powered by radio frequency (rf) energy.[22,23] The supersonic O-atom beam is made from 8% O_2 (vol.), seeded in 92% Argon. The oxygen dissociation rate is ∼40%, as measured by the time-of-flight technique.[24] The radio frequency power was switched on only when the atomic oxygen beam was employed. The absolute oxygen coverages are estimated by comparing them to the saturated coverage (∼2.1 ML), which was obtained in a previous study.[25] One monolayer of oxygen is defined as 1.387×10^{15} atoms/cm^2 and refers to a single atomic layer of close-packed gold. Molecular beams of 2-butanol are generated via the same nozzle as oxygen beams, however the rf power is left off. The integral area under the temperature programmed desorption (TPD) spectra is proportional to the coverage; thus, the absolute coverages of 2-butanol were estimated using the stoichiometry in the partial oxidation reaction. Under certain experimental conditions in which 100% selectivity and yield is achieved, one 2-butanol molecule reacts with one adsorbed oxygen atom to form water and 2-butanone. Using this information, the 2-butanol molecular beam flux has been determined in several experiments to be approximately 0.022 ± 0.004 ML/s. Reagent purity is as follows: 2-butanol (ACROS, anhydrous, 99.0%), $^{16}O_2$ (Matheson Trigas, 99.99%), $^{18}O_2$ (Isotec, 99%), and Argon (Praxair, 99.9%).

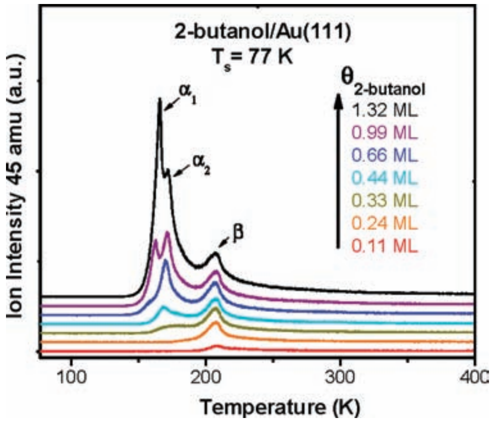

Figure 1. TPD spectra for various 2-butanol coverages on clean Au(111). The heating rate was 1 K/s.

Results and Discussion

Adsorption and Desorportion of 2-Butanol on Clean Au(111). Temperature programmed desorption (TPD) spectra of 2-butanol from the clean Au(111) surface are shown in Figure 1. A number of ion fragments were measured; however, no surface dissociation products were identified during sample heating. Repeated experiments without cleaning between successive measurements showed that the TPD spectra of 2-butanol are highly reproducible. Additionally, Auger electron spectra confirmed that no dissociation products were left on the surface after successive TPD measurements. Thus, we conclude that 2-butanol adsorbs and desorbs molecularly on the Au(111) surface. Only the signals for the most intense fragment of 2-butanol, which has a mass to charge (*m*/*e*) ratio of 45, are shown in Figure 1 for different coverages ranging from ∼0.11 ML to ∼1.32 ML. The TPD spectra show three distinct peaks, which we denote as α_1, α_2, and β. The β peak fills at the lowest coverage and desorbs with a peak at ∼206 K, and therefore is assigned to the 2-butanol monolayer physically adsorbed on the Au(111) surface. Peaks α_1 and α_2, the multilayer features, appear as the 2-butanol exposure increases. The α_2 peak at 170 K represents desorption of a bilayer which is directly associated with the monolayer.[26] The weaker bound multilayer feature, α_1, appears on the shoulder of the α_2 peak at 166 K when the exposure reaches ∼0.66 ML, and begins to dominate the TPD spectra at exposures higher than 1.32 ML (not shown in Figure 1). Using a Redhead analysis,[27] we estimate that the adsorption energy of 2-butanol on Au(111) ranges from ∼41.5 kJ/mol for the multilayer to ∼51.5 kJ/mol for the monolayer. The adsorption energy of 2-butanol is slightly higher than methanol (33.5−38.75 KJ/mol)[13] and ethanol (36.3−45 KJ/mol)[15] but comparable to that of 1-propanol (40.0−49.3 KJ/mol) and 2-propanol (39.3−46.5 KJ/mol).[16]

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The adsorption and thermal chemistry of 2-butanol has been studied on other well-characterized, clean surfaces as well.[28−30] In a TPD study on clean Pt(111) by Lee and Zaera, 2-butanol was converted to 2-butanone, butylene oxide, and butanal.[28] Reflection−absorption infrared spectra (RAIRS) were also acquired and indicate that 2-butanol binds to Pt(111) through the C−O bond which is almost perpendicular to the surface.[28] A series of RAIRS measurements at different temperatures suggest that 2-butoxide, the surface intermediate, forms between 170 and 200 K and then decomposes around 210 K.[28] Similar results were found for clean Pd(111) by Tysoe and co-workers. The key surface intermediate on the Pd(111) surface is suggested to be 2-butoxide via RAIRS measurements.[30] But only a limited portion of 2-butoxide species are converted to 2-butanone via β-hydrogen elimination while the majority of 2-butoxide reforms to 2-butanol, as revealed by TPD experiments.[29]

Reaction of 2-Butanol on Atomic Oxygen Precovered Au(111). At low oxygen precoverages (e.g., $\theta_O = 0.11$ ML) on Au(111), 2-butanol undergoes partial oxidation with high selectivity upon heating, producing 2-butanone and water, along with minor combustion and dehydration products which vary with the O_a/2-butanol ratio. When 0.11 ± 0.02 ML of 2-butanol is coadsorbed with 0.11 ML O_a at 77 K, the selectivity for partial oxidation is 100%, as shown in Figure 2a. The reaction products were identified by comparing the mass to charge (m/e) ratios to the cracking patterns of 2-butanol desorption spectra detailed in previous experiments and also standard spectra from the National Institute of Standards and Technology (NIST). The peak at 188 K for $m/e = 43$ in Figure 2a indicates the formation of 2-butanone. Meanwhile no signal for $m/e = 45$, the most intense fragment of 2-butanol, is observed. The signals for water desorption ($m/e = 18$) expand into a broad peak around 174 K. This peak is close to the desorption temperature of the water formed by hydroxyl disproportionation on Au(111). Previous investigations by Koel et al. (and confirmed by our group and the Friend group) have shown that water interacts strongly with oxygen on Au(111) and desorbs in two peaks on the oxygen precovered Au(111) surface.[14,25,31−33] One peak is at the same temperature as the water desorption peak on the clean Au(111) surface (i.e., ~155 K), while the other is a new peak at 175 K, attributed to the disproportionation of OH on Au(111). Besides 2-butanone and water, we found no other possible oxidation products or coupling species, such as 2-butenal, butanal, butane, 2,3-dimethyloxirane, 2-butanal, butanoic acid, butyl butyrate, ethyl ester, butyric acid, 2-butenoic acid, 3-butenoic acid, methyl propionate, or H_2. Neither C_1−C_3 species, nor CO_2 were detected during exposure of 2-butanol or during the TPD measurements at low oxygen coverages (i. e., up to 0.11 ML). The CO ($m/e = 28$) features between 77 and 140 K are due to desorption of carbon monoxide that has adsorbed onto the sample and other nearby structures (e.g., the Ta support plate for the gold sample) from the residual gases in the scattering chamber, which we refer to hereafter as "background CO". These features appear in several TPD spectra obtained with our apparatus. Since $m/e = 28$ is a cracking fragment of 2-butanone, the peak around 185 K for $m/e = 28$ is assigned to 2-butanone instead of CO. In order to verify the lack of combustion products, we carried out experiments with adsorbed ^{18}O under the same conditions, as shown in Figure 2b. The $m/e = 30$ peak at 184 K is negligible and no $C^{16}O_2$, $C^{18}O^{16}O$, or $C^{18}O_2$ are formed. Thus, we claim that 2-butanol is partial oxidized to 2-butanone with near 100% selectivity under these reaction conditions. The reaction formulary for partial oxidation is

$$C_4H_{10}O + O_a \rightarrow C_4H_8O + H_2O$$

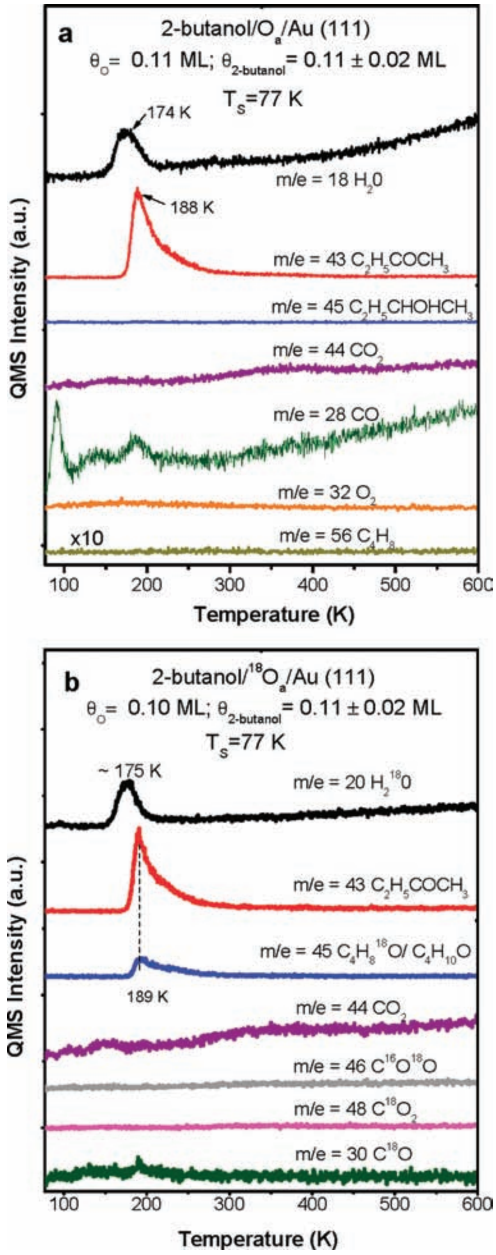

Figure 2. (a) TPD spectra of coadsorbed 2-butanol (0.11 ± 0.02 ML) and $^{16}O_a$ (0.11 ML) from Au (111). The atomic oxygen was dosed first followed by the 2-butanol, both with a sample temperature of 77 K. The heating ramp was 1 K/s. (b) Similar TPD spectra except of coadsorbed 2-butanol (0.11 ± 0.02 ML) and $^{18}O_a$ (0.10 ML).

An extremely interesting phenomenon in our experiments involves oxygen exchange between 2-butanol and adsorbed

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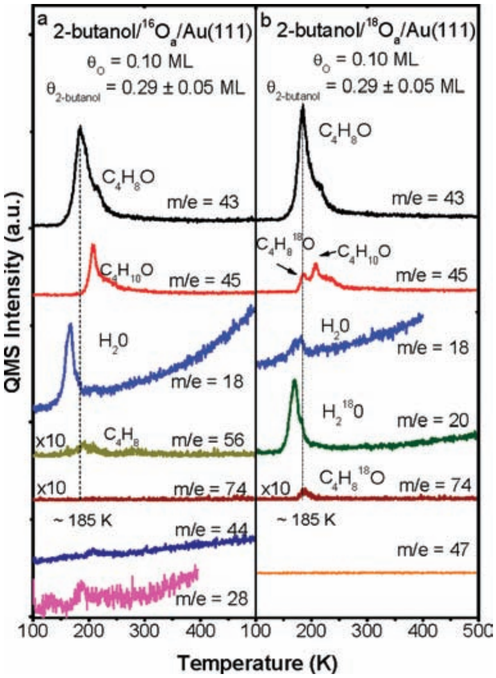

Figure 3. (a) TPD spectra of coadsorbed 2-butanol (0.29 ± 0.05 ML) and $^{16}O_a$ (0.10 ML) from Au (111). The atomic oxygen was dosed first followed by the 2-butanol, both with a sample temperature of 77 K. The heating ramp was 1 K/s. (b) Similar TPD spectra except with an $^{18}O_a$ coverage of 0.10 ML.

oxygen in the formation of 2-butanone. To demonstrate this, we conducted additional TPD experiments with $^{16}O_a$ and $^{18}O_a$ under the same conditions for comparison: 0.29 ± 0.05 ML 2-butanol was dosed on the Au(111) surface precovered with 0.10 ML O_a, and the results are shown in Figure 3. In the $^{16}O_a$ experiments, shown in Figure 3a, multiple products can be identified, including H_2O (m/e = 18), 2-butanone (m/e = 43), and 1-butene or 2-butene (m/e = 56). The CO_2 (m/e =44) peaks are negligible, while the m/e = 28 peak around 185 K is assigned as a fragment of 2-butanone. Because 1-butene and 2-butene have the same cracking pattern, which is similar to that of isobutene, we cannot designate the m/e = 56 peak to a single structure; however, the probability of forming isobutene via reconstruction of carbon chains is slim, since almost no products due to C−C bond cleavage are found. Thus, we deduce that the m/e = 56 peaks come from 1-butene or 2-butene. The unreacted 2-butanol desorbs off the surface during heating, which accounts for the m/e = 45 peak at 207 K, the desorption temperature of 2-butanol on clean Au(111). If a 2-butanol molecule would exchange its ^{16}O atom with adsorbed $^{18}O_a$, $C_4H_8{}^{18}O$ (m/e = 45 or 74) or $C_4H_{10}{}^{18}O$ (m/e = 47) would be expected. In the $^{18}O_a$ experiment shown in Figure 3b, several peaks were detected at 185 K, including m/e = 43, 45, and 74. As discussed earlier, the m/e = 43 peak comes from 2-butanone (C_4H_8O), while the m/e = 45 and 74 signals indicate the formation of $C_4H_8{}^{18}O$ via oxygen scrambling. Thus, we speculate the ^{16}O atom in $H_2{}^{16}O$ is from the hydroxyl group in the 2-butanol. We also note that excess 2-butanol desorbs at 207 K, the same as for the ^{16}O experiment shown in Figure 3a, while no 2-butanol with an ^{18}O atom (m/e = 47) is found.

On the basis of the appearance of multiple products in these two experiments, several possible pathways take place on the oxygen precovered surface, including partial oxidation and dehydration. Since C−O bond cleavage is required to form $C_4H_8{}^{18}O$, 1-butene or 2-butene may serve as the precursor for $C_4H_8{}^{18}O$. However, C_4H_8 was absent under some reaction conditions while $C_4H_8{}^{18}O$ (m/e = 45) occurs around 185 K, the desorption temperature of 2-butanone converted from 2-butanol, as shown Figure 2a. Additional experiments show that the dehydration product (C_4H_8) can only be observed at low O_a coverage ($\theta_O \approx 0.11$ ML) with an O_a/2-butanol ratio of ~0.5. Since the reactivity toward dehydration is very small, the probability for oxygen exchange can be estimated by comparing the signals for $H_2{}^{16}O$ (m/e = 18) to $H_2{}^{18}O$ (m/e = 20). In Figure 3b, $H_2{}^{16}O/H_2{}^{18}O \approx 1:2.8$, which suggests approximately 26% of adsorbed 2-butanol molecules go through the oxygen exchange process.

At higher oxygen coverages ($\theta_O \geq 0.70$ ML), both partial oxidation and full oxidation are possible reaction pathways regardless of 2-butanol coverages. A small amount of CO and CO_2, together with water, were found as combustion products. TPD spectra (Figure S3, Supporting Information) show multiple peaks for water, which are due to different reaction pathways. The O-atoms abstract hydrogen atoms either from the hydroxyl or the carbon backbone, and desorb as water at different temperatures. The 2-butanone peak also broadened, suggesting multiple pathways. No dehydration products were identified.

A series of transient reactive scattering experiments were made at different oxygen coverages between 300 and 400 K, as shown in Figure 4. A beam of 2-butanol was directed onto the O_a precovered Au(111) surface at t = 10 s, and the 2-butanone signal (m/e = 43) appeared promptly. The reaction rate increases to a maximum and then decreases due to the depletion of adsorbed oxygen. The maximum reaction rate increases with higher initial oxygen coverages; however, the higher the initial oxygen coverage, the longer time is needed to reach the maximum rate. The surface temperature also influences the reaction rate. From 300 to 400 K, the maximum reaction rates increase, as shown in Figure 4. Thus, 2-butanol partial oxidation likely has an overall positive activation energy. Considering a simple kinetic model in which 2-butanol first physically adsorbs to the surface, the physisorbed 2-butanol has two pathways to follow at elevated temperatures: reaction (partial oxidation) or desorption. As surface temperature increases, more 2-butanone is observed, which may suggest that the partial oxidation pathway has a larger activation energy than that of desorption.[20,21,34−45] However, in TPD experiments (Figure 2), adsorbed 2-butanone desorbs at ~188 K, a temperature lower than that of 2-butanol (~206 K), which may suggest a lower activation energy for 2-butanone.

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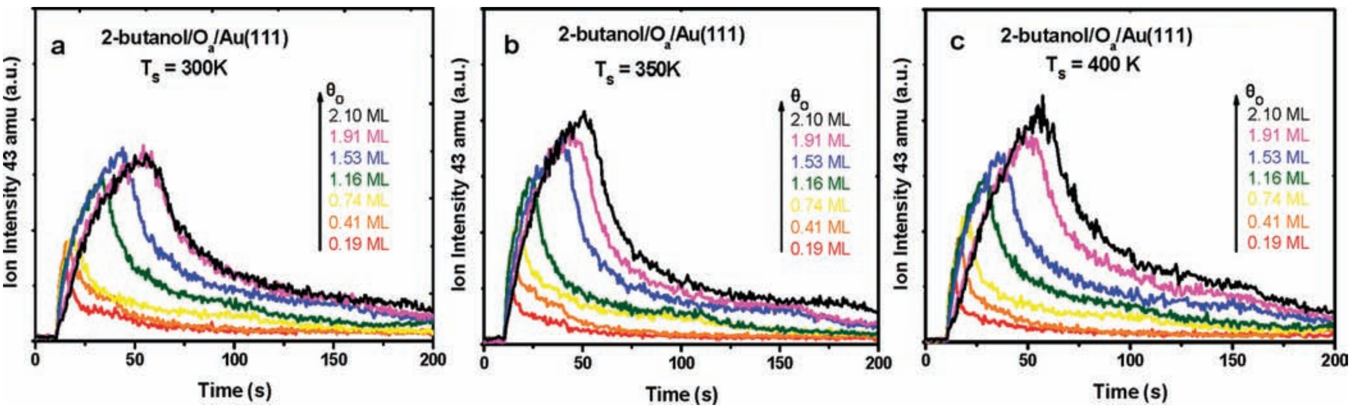

Figure 4. Production of 2-butanone ($m/e = 43$) during reactive scattering measurements of 2-butanol at (a) 300 K, (b) 350 K, and (c) 400 K. At $t = 10$ s, a beam of 2-butanol was dose on the Au(111) surface precovered with various coverages of atomic oxygen. All the graphs employ the same *y* scale.

The results presented here provide information regarding the mechanism for the selective oxidation of alcohols on gold. The atomic oxygen precovered Au(111) surface effectively catalyzes the reaction of 2-butanol into 2-butanone and water, with few side products. Our previous investigations also show high selectivity in the partial oxidation of ethanol, 1-propanol, and 2-propanol under similar conditions to those reported here.[15,16] The experiments with isotope-labeled ethanol (CD_3CH_2OH and C_2H_5OD) demonstrate the cleavage of the O−H and β-C−H bonds.[15] When the O_a covered Au(111) surface is exposed to CD_3CH_2OH at 300 K, only H_2O and CD_3CHO are observed; however, three types of water (H_2O, HDO, and D_2O) occur during C_2H_5OD dosing.[15] Additionally, experiments involving isotopically labeled $^{18}O_a$ suggest that the C−O bonds in ethanol and propanol remain intact.[15,16] As mentioned earlier, we have modified our UHV apparatus with larger beam apertures for the 2-butanol studies reported here leading to an increased signal intensity; thus, the absence of detection of C−O bond cleavage in ethanol and propanol may be due to our lower detection sensitivity for the earlier experiments. Recently, ester formation has been reported in methanol and ethanol oxidation on Au(111),[17,18] but no information about C−O bond cleavage was revealed.

We speculate that two kinds of surface intermediates may form in the reactions of 2-butanol on oxygen covered Au(111): 2-butoxide and η^2-butanone (in which both the α-C and O interact with the surface). The formation of an alkoxide intermediate has been suggested or confirmed in oxidation studies of simple alcohols on other clean and adsorbate-modified surfaces.[46−49] Madix and co-workers performed a series of pioneering investigations on the oxidation of alcohols on the Ag(110) and the Cu(110) single crystal surfaces under UHV conditions.[46−49] On a preoxidized Ag(110) surface, partially deuterated ethanol, CH_3CH_2OD, can be converted to CH_3CHO, C_2H_4, H_2, and D_2O.[46] Employing temperature programmed desorption, only a trace amount of CH_3CHO, observed at 180 K, is formed on the clean Ag(110) surface, but the observed CH_3CHO signal increases dramatically with increasing oxygen coverage. The hydroxyl group of the CH_3CH_2OD molecule probably interacts with the surface oxygen atoms during the adsorption process, leading to the formation of CH_3CH_2O and $D_2{}^{18}O$,[46] while ethoxide is suggested to be the surface intermediate. In addition to TPD, X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were employed to study the oxidation of ethanol on Cu(110).[49] The oxidation of ethanol on Cu(110) shares similar mechanisms with those on Ag(110), except for a few different features.[46] Although ethanol can be oxidized to CH_3CHO on clean Cu(110), the formation of an alkoxy intermediate is promoted on the oxygen covered Cu(110) surface.[49] The ethoxide then decomposes to acetaldehyde and hydrogen.[46] McCash and co-workers performed a RAIRS study of ethanol adsorption on Cu(100) and observed the ethoxide with the C−O bond perpendicular to the surface.[50] Using TPD, XPS, and UPS, Madix et al. also showed that the O−H bond was broken in 1-propanol and 2-propanol forming alkoxy species on both clean and oxygen covered Cu(110) surfaces.[49] On the basis of extensive investigations regarding alcohol oxidation, Madix et al. proposed mechanisms that involve O−H bond cleavage, enhanced by surface oxygen, leading to the formation of an alkoxy intermediate, water, and β-C−H bond activation.[48] Returning to the previously mentioned RAIRS studies by Lee and Zaera on the Pt(111) surface and by Tysoe and co-workers on the Pd(111) surface; this research indicates that 2-butoxide is a surface intermediate in 2-butanol decomposition under UHV conditions.[28,29]

The C−O bond in the 2-butoxide intermediate may be weakened by bonding to the surface, which has been demonstrated in the reaction of 2-propanol on Mo(110).[51] In the surface vibrational spectra, the C−O stretch is shifted to lower energy for 2-propanol adsorbed on Mo(111) compared to gas phase 2-proponal. Propene is formed as the result of C−O bond breaking.[51] Therefore, regarding the experiments reported here, the weakened C−O bond may break in some of the intermediates, which accounts for the formation of C_4H_8 and oxygen exchange between 2-butanone and adsorbed ^{18}O. The formation of $C_4H_8{}^{18}O$ requires the formation and diffusion of transient sec-butyl radicals. Bol and Friend reported both *t*-butyl iodide and *t*-butanethiol react on the Rh(111)-p(2 × 1)-O surface to produce *t*-butanol, isobutene and water via *t*-butyl radicals formed by cleavage of the C−S or C−I bond.[52] So we speculate that transient sec-butyl radicals could form on the oxygen covered Au(111) surface.

Another possible configuration on the surface is η^2-butanone. Although the η^2 state is less preferred on oxygen covered

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surfaces than clean surfaces,[53] it cannot be ruled out on the Au(111) surface precovered with a small amount of adsorbed oxygen. The η^2-aldehyde species may occur after the formation of alkoxides in alcohol oxidations. Davis and Barteau reported that ethanol and 1-propanol form η^2-aldehydes and η^1(C)-acyl, following the alkoxide intermediates on clean Pd (111) under 300 K.[54] They also carried out a TPD study on clean Pd(111) showing that 2-propanol is selectively dehydrogenated to acetone, in addition to decomposition products, such as methane, CO, and H_2.[55] Although the isopropoxide is more stable than the primary alkoxides, the acetone derived from isopropoxide is adsorbed in the η^2 configuration, as revealed by high resolution electron energy loss spectroscopy (HREELS).[54] With both the α-C and O interacting with the surface, portions of the η^2-butanone on Au(111) species may experience C−O bond scission forming C_4H_8 or 2-butanone.

Reaction pathways for alcohol oxidation have also been studied on supported metal particles.[2,56,57] By studying the kinetics of the selective oxidation of aqueous ethanol on a carbon supported platinum catalyst, Van den Tillaart et al. proposed that the first step is the abstraction of the hydroxyl hydrogen of ethanol and the formation of the ethoxide, $CH_3CH_2O_{ads}$.[57] The ethoxy species then react with dissociatively adsorbed oxygen to yield acetaldehyde, meanwhile the hydroxyl species and hydrogen adatoms form water.[57]

The high activity and selectivity of the bulk gold surface may help to elucidate the size-property relationship of gold catalysts. Although small gold nanoparticles (2−4 nm) have high catalytic activity in low temperature CO oxidation as shown by Haruta and Goodman,[58,59] the particle size effect on alcohol partial oxidation remains uncertain.[60] It is possible that both small and large gold particles may contribute to the high selectivity.[1,2,61−63] Our findings are consistent with Biella and Rossi's results on the selective oxidation of alcohols with relatively large Au particles, including 2-butanol.[1] Biella and Rossi tested gold catalysts (1 wt %) supported on silica for 1-propanol oxidation at 573 K. X-ray powder diffraction (XRPD) data showed that the gold particle sizes increased from 15 to 25 nm after 18 h and then remained stable after 60 h.[1] The authors conclude that the catalytic properties are due to relatively large Au clusters supported on silica.[1] Since, the (111) surface is the most abundant surface configuration on the gold nanoparticles, the Au(111) surface may account for the high selectivity of the relatively large gold nanoparticles. In addition, Abad and co-workers carried out a systematic study on the particle size effect of supported gold catalysts.[62] By studying cinnamyl alcohol oxidation using Au/TiO_2, they demonstrate that selectivity is independent of gold particle size, although turnover frequencies decrease exponentially with the increase in particle size.[62] In their study, the sizes of gold particles on TiO_2 ranged from 5 to 25 nm. Thus, the oxygen precovered Au (111) surface under UHV conditions could serve as a useful model catalyst in future studies of the partial oxidation of alcohols.

Conclusions

In this paper, we have presented the results of an investigation of the selective oxidation of 2-butanol on the atomic oxygen precovered Au(111) surface. The 2-butanol molecule adsorbs and desorbs reversibly on the clean Au(111) surface. However, atomic oxygen precovered bulk gold shows high reactivity and selectivity in partially oxidizing 2-butanol into 2-butanone and water at low oxygen coverages ($\theta_O \leq 0.11$ ML). Isotope experiments show that 2-butanol ($C_4H_{10}{}^{16}O$) can exchange its ^{16}O atom with an adsorbed $^{18}O_a$, producing ^{18}O containing 2-butanone ($C_4H_8{}^{18}O$). This oxygen exchange phenomenon indicates C−O bond cleavage during the reaction. Besides partial oxidation, combustion and dehydration products can be found along with 2-butanol and water. At higher oxygen coverages ($\theta_O \geq 0.70$ ML), both partial oxidation and combustion are active. Employing previous results regarding the selective oxidation of simple alcohols on Au(111) and other surfaces, we propose two kinds of surface intermediates: 2-butoxide and η^2-aldehyde.

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Supporting Information Available: The oxidation reactions of 1-butene and 2-butene on oxygen precovered Au(111) are presented. TPD spectra of 2-butanol oxidation at higher oxygen coverages ($\theta_O \geq 0.70$ ML) are also included. This material is available free of charge via the Internet at http://pubs.acs.org.

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