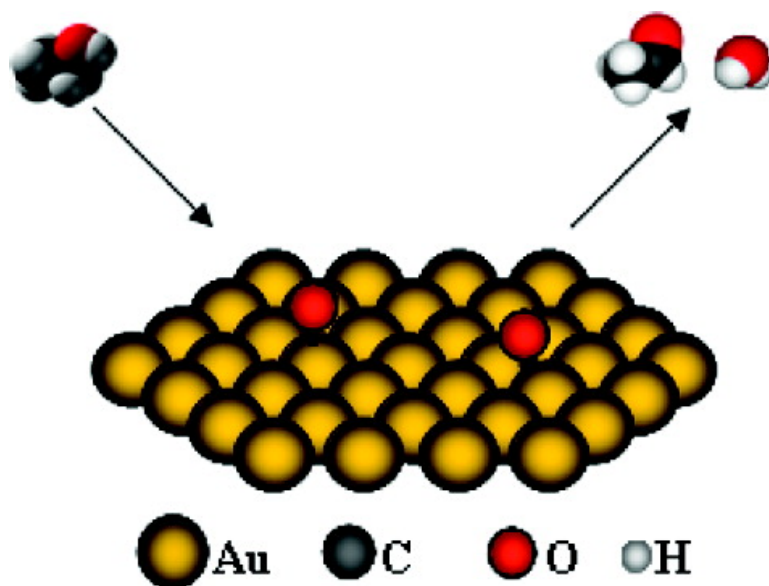


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## Selective Oxidation of Ethanol to Acetaldehyde on Gold

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The selective oxidation of alcohols is both technologically and fundamentally important and has attracted significant attention recently.<sup>1</sup> In particular, ethanol is considered to be a promising renewable resource for replacing decreasing petrochemical reserves. Ethanol can be produced from biomass via fermentation with possible applications in alternative fuels, solvents, fuel cells, and as a feedstock for producing bulk chemicals via selective oxidation.<sup>2</sup> Compared to studies over high-surface-area catalysts,<sup>3,4</sup> studies conducted in ultrahigh vacuum (UHV) can provide additional mechanistic details. Previous fundamental investigations on the oxidation of ethanol have focused on Pt,<sup>5,6</sup> Rh,<sup>7</sup> Pd,<sup>8,9</sup> and Mo<sup>10</sup> single crystals; studies of coinage metals included Cu(110) and Ag(110).<sup>11</sup>

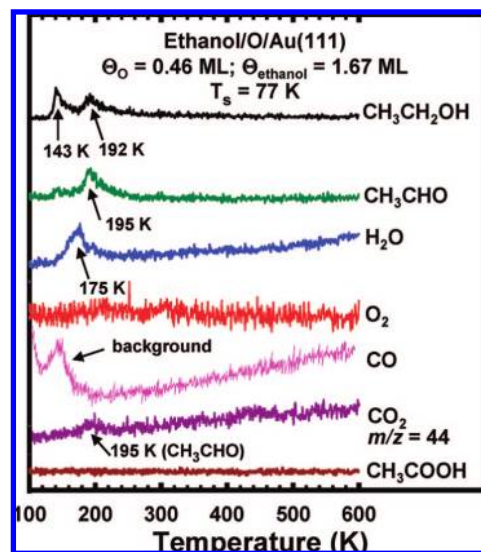
Increasing interest in gold catalysis can be partly attributed to two seminal discoveries: catalytic oxidation of CO by Haruta et al.<sup>12</sup> and hydrochlorination of acetylene by Hutchings et al.<sup>13</sup> Reactions that can be effectively catalyzed on both gold nanoparticles (NPs) and macroscopic gold are of great interest considering the notable size dependencies for some conversions.<sup>2,14–22</sup> Recently, it has been found that supported Au clusters are selective and stable for oxidation of various alcohols to their corresponding aldehydes/acids and ketones.<sup>2,22,23</sup> Importantly, Biella and Rossi have shown that relatively large gold NPs (> 15 nm) supported on silica can effectively catalyze volatile alcohols to aldehydes and ketones with very high selectivity.<sup>23</sup> These results, in part, have motivated us to explore the oxidation chemistry of alcohols on macroscopic gold.<sup>24,25</sup>

Herein we present results of the oxidative conversion of ethanol into acetaldehyde on Au(111) employing temperature-programmed desorption (TPD) and molecular beam reactive scattering (MBRS). Our results show that ethanol initially undergoes O–H bond cleavage (producing ethoxide) followed by selective  $\beta$ -C–H bond ( $\alpha$  to the oxygen) activation to form acetaldehyde and water on atomic oxygen precovered Au(111). The results may provide insight into reaction mechanisms of alcohols on high-surface-area metal-oxide-supported Au catalysts.

The experiments were performed in a molecular beam surface scattering chamber that has been described elsewhere,<sup>15,24,26</sup> but particularly pertinent details are described in Supporting Information. CH<sub>3</sub>CH<sub>2</sub>OH (Fisher Scientific, 99.5%), CH<sub>3</sub>CH<sub>2</sub>OD (Cambridge Isotope Laboratories, 99% D), CD<sub>3</sub>CH<sub>2</sub>OH (Cambridge Isotope Laboratories, 98% D), <sup>16</sup>O<sub>2</sub> (Matheson Trigas, 99.99%), <sup>18</sup>O<sub>2</sub> (Isotec 99.7%), and Ar (Praxair, 99.9%) were used without further purification and their purities were confirmed by mass spectrometry.

On clean Au(111), ethanol weakly adsorbs and desorbs molecularly. Repeated exposures provide reproducible TPD spectra and Auger electron spectra confirm that no dissociation products (i.e., residual carbon, and/or surface bound oxygen) remain on the surface. The ethanol coverages are defined relative to the integral area under the desorption curves of saturated monolayer states (peak

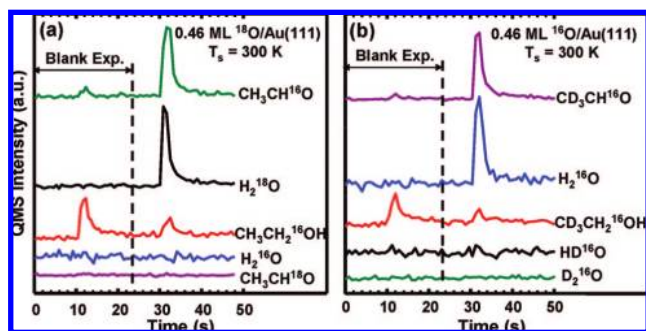
at ~180 K shown in Figure S1). Desorption peaks at lower temperatures (~145 K) correspond to multilayers and grow indefinitely with ethanol exposure.



**Figure 1.** Temperature-programmed desorption spectra following adsorption of 1.67 ML ethanol on Au(111) at 77 K with atomic oxygen precoverages of  $\theta_{\text{O}} = 0.46$  ML. The spectra were acquired at a ramp rate of 1 K/s. Atomic oxygen was dosed at 77 K.

Figure 1 shows TPD spectra of ethanol oxidation following adsorption of 1.67 monolayers (ML) of ethanol on Au(111) at 77 K with an atomic oxygen precoverage of  $\theta_{\text{O}} = 0.46$  ML. Oxidation is indicated by the formation of acetaldehyde (in addition to water) with 100% selectivity. No other partial oxidation products, such as methane (CH<sub>4</sub>), ethane (H<sub>3</sub>CCH<sub>3</sub>), ethylene (H<sub>2</sub>C=CH<sub>2</sub>), ethenol (H<sub>2</sub>C=CH–OH), acetic acid (H<sub>3</sub>CCOOH), ethylene oxide, methyl formate (HCOOCH<sub>3</sub>), and ethyl acetate (H<sub>3</sub>CHCOOC<sub>2</sub>H<sub>5</sub>) were detected either during the ethanol impingement phase of the experiments or during subsequent TPDs. No CO, CO<sub>2</sub> (Figure 1 and Figure S2), formaldehyde, or formic acid are detected. As shown in Figure 1, acetaldehyde desorption produces a peak at ~195 K. Water is generated and desorbs with a peak at ~175 K which can be ascribed to hydroxyl recombination.<sup>27,28</sup> Hydroxyl groups are formed via the surface reaction of atomic oxygen and hydroxyl hydrogen in an ethanol molecule as also reported on Cu(110) and Ag(110).<sup>11</sup> Indeed, the abstraction of acidic hydrogen has been reported on atomic oxygen precovered gold previously for water,<sup>27,28</sup> ammonia,<sup>21</sup> ethylene,<sup>29</sup> methanol,<sup>24</sup> and propanol<sup>25</sup> and is commonly ascribed to the Brønsted-base character of oxygen adatoms on the group 1B metals (Note that methanol is fully oxidized to form H<sub>2</sub>O, CO, and CO<sub>2</sub> on Au(111) regardless of oxygen coverage<sup>24</sup>). A mass balance confirms stoichiometric consumption of ethanol by reaction with surface-bound atomic

oxygen exclusively producing acetaldehyde and water, indicating this reaction pathway  $C_2H_5OH + O_a \rightarrow CH_3CHO + H_2O$ . As will be presented later, the acetaldehyde production results from a  $\beta$ -hydride elimination ( $\alpha$  to the oxygen) step from a surface-bound ethoxide species. Additionally, we investigated the influence of atomic oxygen coverage on oxidation product distribution. We found that, at high oxygen coverages (i.e., greater than 1.0 ML), in addition to acetaldehyde and water,  $CO_2$  was also formed during the reaction due to the cleavage of the  $\gamma$ -C–H bond and the C–C bond (Figure S3). The change in product distribution could be due to the changed chemical state of atomic oxygen (i.e., from chemisorbed surface oxygen at low coverage to an oxide phase at high coverage<sup>30</sup>).



**Figure 2.** Evolution of acetaldehyde and water from (a)  $C_2H_5OH$  impingement on  $^{18}O_a$  precovered Au(111) at 300 K ( $t = 30$  to  $32$  s); (b)  $CD_3CH_2OH$  impingement on  $^{16}O_a$  precovered Au(111) at 300 K ( $t = 30$ – $32$  s). Atomic oxygen is deposited on Au(111) at 77 K with a coverage of  $\sim 0.46$  ML. A blank experiment is shown from  $t \approx 10$ – $12$  s where an ethanol beam is impinged on an inert-stainless-steel flag placed in front of the Au(111) surface. The sample is heated to 300 K prior to impinging a continuous ethanol beam on the surface.

To further explore the details of the reaction, that is, reaction pathways toward acetaldehyde formation, we investigated possible C–O bond cleavage employing MBRS measurements using isotopically labeled  $^{18}O$  at surface temperatures from 300 to 400 K. These temperatures lie above the desorption temperatures of ethanol, water, and acetaldehyde as well as possible surface intermediates (i.e., ethoxide) (to prevent accumulation of species on the surface) but well below the onset of recombinative oxygen desorption ( $\sim 460$  K). Figure 2a displays a representative MBRS experiment performed at 300 K on Au(111) with a 0.46 ML of  $^{18}O$  predeposited at 77 K. Results of a blank experiment are shown from  $t \approx 10$ – $12$  s in which the ethanol beam is impinged on an inert-stainless-steel flag placed in front of the Au(111) sample. Only ethanol evolution was observed with  $m/z$  31 (red) and 29 (green). From  $t \approx 30$ – $32$  s, the ethanol beam is impinged on  $^{18}O$ -covered Au(111) and the water and acetaldehyde production are monitored with the QMS. We observed that only  $CH_3CH^{16}O$  and  $H_2^{18}O$  evolved upon ethanol impingement. No  $CH_3CH^{18}O$  or  $H_2^{16}O$  were detected, indicating the absence of C–O bond cleavage. Notably, the conversion rate of ethanol is about 65%.

The presence of an intact C–O bond facilitates cleavage of  $\beta$ -C–H bonds to the metal in formed alkoxides.<sup>9</sup> Cleavage of  $\beta$ -C–H and  $\gamma$ -C–H bonds were also investigated employing deuterated ethanol,  $CD_3CH_2OH$ , and  $C_2H_5OD$ . Figure 2b presents evidence of the lack of  $\gamma$ -C–H bond breaking during the reaction. Upon impingement of  $CD_3CH_2OH$  on 0.46 ML  $^{16}O_a$  precovered Au(111) at 300 K, only  $H_2O$  and  $CD_3CHO$  were observed. No  $D_2O$  or  $HDO$  were evolved during the  $CD_3CH_2OH$  impingement. In a similar reactive scattering experiment (Figure S4), we impinged a

continuous  $C_2H_5OD$  beam on a 0.46 ML  $^{16}O_a$  precovered Au(111) where the surface temperature was held at 300 K. Three types of water ( $D_2O$ ,  $HDO$ , and  $H_2O$ ) were observed during impingement of the  $C_2H_5OD$  beam. This result combined with those from Figure 2b strongly suggests that both the  $\beta$ -C–H and O–H bonds are cleaved in selective oxidation of ethanol to acetaldehyde while nonselective  $\gamma$ -C–H bonds stay intact.

In conclusion, we have presented experimental evidence of selective oxidation of ethanol to acetaldehyde on atomic oxygen precovered Au(111). Results from isotopic experiments show that ethanol initially undergoes O–H bond cleavage (producing ethoxide) followed by selective  $\beta$ -C– bond ( $\alpha$  to the oxygen) activation to form acetaldehyde and water. These results could provide insights into reaction mechanisms of alcohols on high-surface-area supported Au catalysts (e.g., active sites, elementary steps involving activated oxygen species).

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**Supporting Information Available:** Experimental details and Figures S1–S4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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