VIP Alcohol Oxidation

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Selectivity Control in Gold-Mediated Esterification of Methanol**

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Interest in catalysis by gold has undergone a tremendous resurgence owing to its great potential in the development of environmentally friendly processes. Following research on gold catalysis in the 1970s,[1] this area of study lay fallow until Haruta and colleagues showed that catalytic oxidation of CO to CO_2 by gold nanoparticles using gaseous O_2 was significantly improved by supporting the nanoparticles on Fe_2O_3.[2] Since then, a flurry of research activity has focused on understanding the basis for the activation of gold.[3] Furthermore, a wide range of reactions have been shown to be promoted by gold catalysts under a variety of conditions, including recent studies showing that gold supported on reducible oxide supports catalyzes the aerobic oxidation of alcohols in solution.[4–10] Aerobic oxidation of alcohols using gold catalysts affords the possibility of producing carbonyl derivatives with an environmentally benign process that could replace the current technology that uses heavy-metal salts as oxidizing agents.[10] The catalytic oxidation of alcohols is also important in the development of fuel cells[11] and in the synthesis of esters used as fragrances and flavoring.

To achieve high reaction efficiency and exploit new catalytic systems, it is important to understand the mechanism of the oxidation reactions over gold catalysts at a molecular level. Under practical catalytic conditions, reducible metal oxide supports, for example, TiO_2, are present.[12,13] To fully understand the efficacy of gold for selective oxidation catalysis, elucidation of the intrinsic chemistry of gold, without the support material, is critical.

Fundamental studies using well-defined systems under ultrahigh vacuum (UHV) conditions provide insight into the mechanisms of catalytic processes.[14–16] Generally, oxidation reactions require the presence of adsorbed atomic oxygen. The rates of oxidation reactions depend on the rate of activation of O_2, which is generally extremely low;[17] nevertheless, fundamental studies of oxygen atoms bound to Au(111), formed by exposure to ozone,[18] provide insight into the ensuing elementary steps. Under the conditions used herein, oxidation of Au(111) by ozone at a surface temperature of 200 K promotes the formation of gold nanoclusters, 80% of which have diameters of approximately 2 nm, on which oxygen atoms are bound.[19] Furthermore, the local bonding environment for oxygen depends on its coverage.[20] For low oxygen coverages and for oxidation at 200 K, a single predominant vibration at approximately 370 cm^{-1} is observed in high-resolution electron energy loss (HREEL) spectra.[21]

Herein, we show that the Au–O surface prepared in this manner promotes the conversion of methanol to methyl formate, formaldehyde, and formic acid. Remarkably, the esterification reaction to form methyl formate and all competing reactions occur below 300 K (at 220–280 K), revealing them to be very facile. No reconstruction of the Au–O nanostructures formed at 200 K is expected in the time taken to heat to 280 K (ca. 5 s). Even at 300 K only minimal changes in the nanoparticles are observed by STM after 30 min. Furthermore, esterification only occurs at oxygen coverages below 0.5 monolayers (ML), and the overall reactivity of the surface decreases at higher oxygen coverages.

At low oxygen coverages (below 0.5 ML), methyl formate ($HCOOCH_3$, m/z 60) and formaldehyde (HCHO, m/z 30) are evolved at 220 and 250 K, respectively (Figure 1a). Methanol is released in a peak centered at 220 K that is coincident with the evolution of methyl formate. When the initial oxygen coverage is above 0.1 ML, O_2 desorption is also detected at approximately 540 K, the temperature characteristic of oxygen-atom recombination on Au(111). Formic acid (HCOOH, m/z 46), CO_2, and H_2O are also liberated

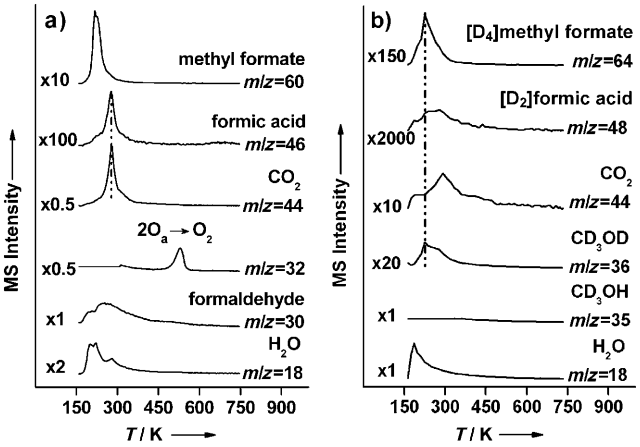

Figure 1. Temperature-programmed reaction (TPR) spectra for a) CH_3OH on O/Au(111) ($\theta_o = 0.2$ ML) and b) CD_3OH ($\theta_o = 0.05$ ML). Oxidation by ozone was conducted at 200 K. The contribution from fragmentation of methanol (CH_3OH in (a) and CD_3OH in (b)) was subtracted for clarity. No reaction is detected on clean Au(111). The heating rate was approximately 10 $K\,s^{-1}$.

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concomitantly at 280 K, indicating that they must originate from the same intermediate in the same rate-limiting step.

To assist in the identification of the reaction intermediate (or intermediates), temperature-programmed reaction was performed with CD_3OH (Figure 1b). Analogous to CH_3OH, [D_4]methyl formate and [D_4]MeOH are evolved concomitantly, primarily at 230–240 K. The simultaneous evolution of CD_3OD and $DCOOCD_3$ is a clear signature for C–D(H) bond cleavage in methoxy as the rate-determining step for ester formation (see below). The temperature difference between formation of [D_4]methyl formate and [D_0]methyl formate from CD_3OD and CH_3OH, respectively, of +10–15 K for the oxidation is also consistent with the kinetic isotope effect expected for C–H bond activation as the rate-limiting step.[22] The activation energy for the formation of the methyl formate is estimated to be approximately 13 kcal mol^{-1} on the basis of the peak temperature of 220 K, assuming a pre-exponential factor of 10^{13} s^{-1}.

To verify that the rate of methyl formate evolution is limited by reaction, [D_0]methyl formate was coadsorbed with [D_4]MeOH on the oxygen-predosed (200 K) Au(111) surface. Ester evolution is clearly limited by reaction, since the desorption peak temperature of [D_0]methyl formate (185 K) is 50 K lower than the peak temperature for producing [D_4]methyl formate from oxidation of [D_4]MeOH (235 K; Figure S1 in the Supporting Information). This difference cannot be explained by the kinetic isotope effect, which is +10–15 K for the oxidation of CD_3OH versus CH_3OH, as noted above.

The selectivity for methyl formate synthesis from CH_3OH is highest for low oxygen coverages, as shown by the ratio of the peak intensity of methyl formate to CO_2 as the initial oxygen coverage is varied for a fixed methanol exposure (Figure 2). At high coverages (e.g. 1 ML), total combustion to CO_2 and H_2O predominates, and no methyl formate or formic acid is detected.

The fraction of adsorbed oxygen that reacts with methanol is also highest at low oxygen coverages, judging from the amount of residual oxygen on the surface, as determined from the integrated intensity of the O_2 peak at 540 K.[18] For an initial oxygen coverage of 0.2 ML, approximately 20% (0.035 ML) of the oxygen remains, whereas about 40% remains after reaction for an initial oxygen coverage of 0.5 ML, and approximately 80% of the oxygen is left behind after reaction for a saturation coverage of 1.0 ML (Figure 2).

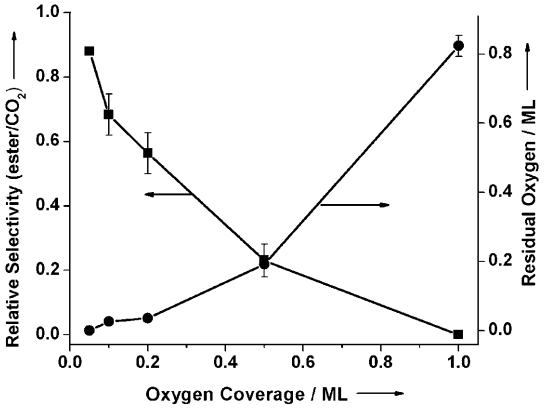

Figure 2. Relative selectivity for methyl formate (■, the ratio (m/z 60):(m/z 44) corrected for cracking fraction) versus initial oxygen coverage. Also shown is the amount of residual oxygen that desorbs near 540 K (●). Ozone was dosed at a surface temperature of 200 K.

Vibrational (HREEL) spectroscopy was used to identify the surface species isolated by heating to selected temperatures (Figure 3 and Table S1 in the Supporting Information). Assignments are based on reference data for reactions of

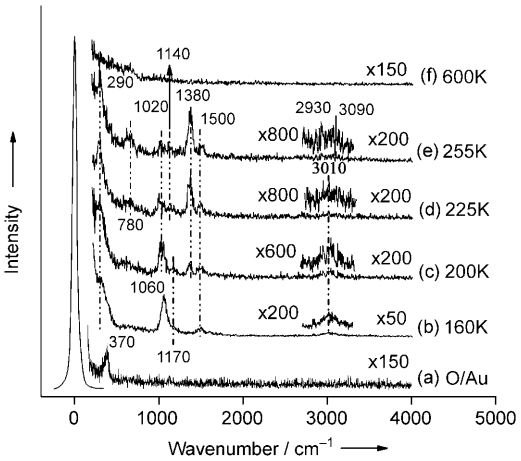

Figure 3. Vibrational spectra of intermediates formed during the reaction of methanol with O/Au(111). a) As-prepared O/Au(111) with 0.1 ML atomic oxygen deposited from ozone at 200 K (O/Au); b) after exposure to methanol at 160 K; c) after heating the methanol layer to 200 K, d) 225 K, e) 255 K, and f) 600 K. All spectra were collected at 160 K. The full width at half maximum (FWHM) for the elastic peaks is 60 cm^{-1}.

methanol and formaldehyde on Cu(110).[23] A peak with frequency of 370 cm^{-1} is observed after oxidation at 200 K for an oxygen coverage of 0.1 ML. It is attributed to oxygen atoms chemisorbed on three-fold sites on the clusters.[19,21] After exposure of this surface to methanol, this peak shifts to the lower-frequency region, similar to the downshift observed for methoxy from methanol on Cu(110).[23] Figure 3 indicates that methoxy is formed upon exposure of the preoxidized surface to methanol at 160 K. If intact methanol were present, a feature near 740 cm^{-1} would be observed. The vibrational peaks at 1060, 1170, 1500, and 3010 cm^{-1} are assigned to ν_{C-O}, ρ_{C-H}, δ_{C-H}, and ν_{C-H} for the CH_3O moiety. Upon annealing to 200 K, the features for methoxy diminish in intensity as methanol and methyl formate are evolved from the surface. A peak at 1380 cm^{-1} emerges that is characteristic of the O-C-O symmetric stretch in formate.[24] Further annealing to 225 and 255 K produces peaks at 780, 1380, and 1500 cm^{-1} that are readily assigned to formate. The formate features are absent with heating to 290 K, and the clean surface is regenerated after annealing to 600 K. The broad feature near 660 cm^{-1} that is observed in all spectra could be due to a trace amount of surface impurity that is undetectable by Auger electron spectroscopy.

The isotopic identities of the methyl formate and methanol evolved concomitantly clearly show that adsorbed methoxy is directly involved in their formation. This deduction is further substantiated by the vibrational spectrum

(Figure 3b) and is similar to previous studies in which activation of alcohols is initiated by the Brønsted acid–base reaction between the protons in the OH group and surface oxygen atoms,[25,26] as in the reaction in Equation (1).

$$2\,CH_3OH_{(a)} + O_{(a)} \rightarrow 2\,CH_3O_{(a)} + H_2O_{(g)} \quad (1)$$

On the basis of studies of copper and silver, the reaction expected for adsorbed methoxy is C–H bond cleavage to form adsorbed formaldehyde and atomic hydrogen, as in Equation (2).

$$CH_3O_{(a)} \rightarrow H_2CO_{(a)} + H_{(a)} \quad (2)$$

The observed isotope effect is consistent with this step being rate-limiting. Ester formation then follows from Equation (3).

$$HCHO_{(a)} + CH_3O_{(a)} \rightarrow HCOOCH_{3\,(g)} + H_{(a)} \quad (3)$$

The hydrogen released reacts via two pathways [Eqs. (4) and (5)].

$$H_{(a)} + CH_3O_{(a)} \rightarrow CH_3OH_{(a)} \rightarrow CH_3OH_{(g)} \quad (4)$$

$$2\,H_{(a)} + O_{(a)} \rightarrow H_2O_{(a)} \rightarrow H_2O_{(g)} \quad (5)$$

To further confirm the reaction mechanism, formaldehyde was introduced onto the surface precovered with methoxy. A substantial increase in the amount of methyl formate was observed (Figure S2 in the Supporting Information), with an ester/CO_2 ratio of 1.8, as compared to 0.9 in Figure 2, thus clearly demonstrating the reaction pathway. It is noteworthy that the same esterification pathway has been observed on Ag(110)[25] and Au(110)[26] surfaces.

Formate is indicated as the reactive intermediate leading to the formation of both formic acid and CO_2, as they originate with the same kinetics. The decomposition of formate has been extensively studied on coinage-metal surfaces. In the absence of excess adsorbed oxygen, it yields CO_2, H_2, and formic acid. Depending on the rate of reaction of formate with adsorbed H, the distribution between H_2 and formic acid varies. With excess adsorbed oxygen, H_2O is observed in place of H_2.[27,28] It is also known that adsorbed formate can be produced by reaction of formaldehyde with adsorbed oxygen on Au(110).[28] Reaction of formaldehyde with oxygen at low coverages on Au(111) produces the same features of formic acid and CO_2 as observed in Figure 1, indicative of the formation of formate in the reaction of methanol with preadsorbed oxygen on Au(111). Vibrational spectra are used to verify the presence of formate (Figure 3e). Its formation is further support for the involvement of transient adsorbed formaldehyde in the reaction. We therefore suggest the following sequence of steps [Eqs. (6)–(8)].

$$HCHO_{(a)} + O_{(a)} \rightarrow HCOO_{(a)} + H_{(a)} \quad (6)$$

$$HCOO_{(a)} \rightarrow CO_{2(g)} + H_{(a)} \quad (7)$$

$$HCOO_{(a)} + H_{(a)} \rightarrow HCOOH_{(a)} \rightarrow HCOOH_{(g)} \quad (8)$$

Again, surface H can be scavenged as in Equation (5).

Since the activation of methanol to form methoxy is the initial step in the sequence, oxygen adsorbed at the three-fold sites at low coverage appears responsible for the overall reactivity. At higher oxygen coverages, the surface is more ordered, and other O bonding configurations are present.[20] This result has important implications for industrial catalysis, suggesting that the effective surface concentration of activated oxygen must be kept very low to achieve steady reactivity and to prevent surface deactivation.

Previous studies of methanol oxidation on two different extended gold surfaces differ in the reported product distributions. In the first case, methyl formate was suggested to form in the reaction of methanol on O-covered Au(110),[26] indicating that esterification can be promoted by extended Au surfaces. The bonding of O to Au(110) was not studied in detail or varied. More recently, combustion was reported as the sole reaction, and no ester formation was detected on Au(111).[29] There are three important differences between these studies and the work discussed herein. First, the method for oxidation of the Au(111) surface was different, possibly leading to differences in the bonding environment of the oxygen: a radio-frequency plasma jet was used. Secondly, and possibly more importantly, in the study in which no esterification was observed, methanol was exposed to the surface at a temperature (77 K) too low for water desorption,[29] compared to a dosing temperature of 160 K—close to the temperature where water leaves the surface—in our experiments. Finally, in the other studies, the extent of reaction appears to be low, so the methyl formate may have gone undetected.

In conclusion, by combining temperature-programmed reaction with vibrational spectroscopy, we have established important mechanistic features of methanol oxidation over gold. Brønsted acid–base reaction between methanol and surface oxygen initiates the reactions, generating surface methoxy. The low-temperature formation of the ester proceeds by the reaction of formaldehyde generated by C–H bond cleavage in the methoxy with another methoxy moiety. Formaldehyde also reacts with adsorbed oxygen to produce adsorbed formate, which in turn produces CO_2 and HCOOH. The oxygen coverage, the bonding environment of oxygen, and the desorption of water appear to play essential roles in gold-mediated oxidation reactions.

Experimental Section

Clean Au(111) was prepared as described previously.[20] All TPR studies were conducted with well-established protocols.[20] The reaction products were identified by quantitative mass spectrometry (Hiden HAL/3F) using fragmentation patterns obtained from authentic samples. Identification was aided by the mass shifts observed with isotope-labeling using [D_4] and [D_3]MeOH as reactants. HREEL experiments were performed with an LK2000 spectrometer using a primary energy of 7.17 eV at 60° specular geometry. Ozone exposure to the Au(111) surface at 200 K was used to deposit atomic oxygen prior to exposure to methanol. The initial surface concentration of atomic oxygen was reproducibly varied by controlling the ozone flux. After exposure of the oxygen-covered Au(111) surface to methanol at 160 K, temperature-programmed

reaction was employed to identify reaction products and to interrogate the mechanism of the reactions.

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