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# Origin of the selectivity in the gold-mediated oxidation of benzyl alcohol

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# ABSTRACT

Benzyl alcohol has received substantial attention as a probe molecule to test the selectivity and efficiency of novel metallic gold catalysts. Herein, the mechanisms of benzyl alcohol oxidation on a gold surface covered with atomic oxygen are elucidated; the results show direct correspondence to the reaction on gold-based catalysts. The selective, partial oxidation of benzyl alcohol to benzaldehyde is achieved with low oxygen surface concentrations and takes place through dehydrogenation of the alcohol to form benzaldehyde via a benzyloxy ( $C_6H_5$ – $CH_2O$ ) intermediate. While in this case atomic oxygen plays solely a dehydrogenating role, at higher concentrations it leads to the formation of intermediates from benzaldehyde, producing benzoic acid and CO<sub>2</sub>. Facile ester (benzyl benzoate) formation also occurs at low oxygen concentrations, which indicates that benzoic acid is not a precursor of further oxidation of the ester; instead, the ester is produced by the coupling of adsorbed benzyloxy and benzaldehyde. Key to the high selectivity seen at low oxygen concentrations is the fact that the production of the aldehyde (and esters) is kinetically favored over the production of benzoic acid.

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# 1. Introduction

Gold-based heterogeneous catalysis has been an intense area of research in the recent years [1–5]. The propitious effort in this area is related to the search for environmentally friendly synthetic processes, where organic solvents are not necessary, innocuous oxidants (e.g. oxygen, air, hydrogen peroxide) are employed, and renewable energy sources can be used (e.g. through photocatalysis). Remarkably, two desired characteristics in modern catalysis, *cleaner reactions* and *less expensive processes*, are combined exceptionally for gold-based catalysis.

Although the underlying principles behind the oxygen-assisted activity of gold are emerging [1,5,6], the complexity of the supported catalyst still presents challenges for complete understanding. In particular, the details regarding the activation of molecular oxygen  $(O_2)$  remain unclear for both supported and unsupported gold catalysts. Recent experiments with nanoporous (unsupported) gold show high activity and selectivity for alcohol esterification and suggest that the catalytic activity, in particular the activation of molecular oxygen, may be closely linked to under-coordinated gold surface atoms [7,8]. The reactions observed were entirely predicted from our previous studies under controlled conditions (using ultra high vacuum methods) [9] and parallel the results obtained in the liquid phase at practical catalytic conditions as well [10].

We have elucidated the mechanism of several gold-mediated oxidation reactions, using gold surfaces pre-covered with atomic oxygen under ultra-high vacuum (UHV) conditions [9–22]. The generation of atomic oxygen on the surface provides active oxidant species which activate many substrates containing acidic hydrogen. Under these conditions the atomic oxygen also induces the formation of gold nanoparticles on the originally ordered Au(111) surface [15,22–25]. The use of UHV conditions allows for a controlled environment in which the concentration of reactants and the nature of the surface can be monitored with high precision. As noted above these studies correlate well with the results of other investigations conducted under more practical working conditions where direct comparisons are possible [7–10,26,27].

The oxidation of benzyl alcohol is a test reaction for probing the properties of novel gold-based catalysts [28-70]. The work reported here focuses on the mechanism for this reaction. Although the use of benzyl alcohol as a probe is partially motivated by the importance of its oxidation products (benzaldehyde, benzoic acid and benzyl esters) in the fragrance and food industries, it possesses unique physical and chemical properties attractive for practical studies. Since this alcohol does not form allotropes with water (as it is the case for most aliphatic alcohols), its purity is advantageous for studying solvent-free catalysis [29-36,44-49,58,59]. Further, due to its relatively high boiling point, the reaction can be studied over a broad temperature span without phase changes. Chemically, a consistent pattern of reactivity over a wide variety of gold-based catalysts is observed, characterized by an extremely selective conversion to benzaldehyde (~90%) [31-40,44-46,54-62]. Limited amounts of benzyl benzoate are usually detected, and benzoic acid is often undetected. This fact has been explained by assuming that the acid readily undergoes a

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condensation reaction with the alcohol, forming the ester and eliminating water, even in solvent-free conditions [30–33,45–47,59]. While condensation can be expected in solution, the present work demonstrates that in a solvent environment the production of ester and acid take place through different mechanisms, with the latter being kinetically more demanding.

## 2. Experimental section

Experiments were performed in a chamber with a base pressure below  $2 \times 10^{-10}$  Torr, equipped with a mass spectrometer (Hiden HAL 3F) and an electron-energy loss spectrometer (LK 2000). In addition, the chamber is outfitted with an Auger electron spectrometer (PHI 15–155) and low-energy electron diffraction optics (PHI 15–120), which are employed to determine the cleanliness and morphology of the Au(111) surface.

The gold surface was routinely cleaned by cycles of ozone  $(O_3)$  exposure at 200 K followed by an annealing to 600 K; the temperatureprogrammed desorption of a clean surface treated with  $O_3$  is characterized by the sole evolution of  $O_2$  at 540 K [23]. Once this is verified, the clean surface is annealed to 900 K for 10 min to achieve the herringbone reconstruction characteristic of a flat Au(111) surface [13,23]. When the surface contamination is significant (appearing clearly in AES or distorting the LEED pattern), Ar<sup>+</sup> sputtering/annealing cycles were employed.

Oxidation experiments were done by first populating the surface with atomic O through the introduction of an appropriate amount of O<sub>3</sub> at 200 K. Briefly, ozone was dosed from a trap maintained near 190 K by an alcohol/dry ice cooling bath [13,71]. The coverage of atomic O is determined by referencing the amount of O<sub>2</sub> evolving during the TPRS of the oxygen-covered surface (hereafter denoted as O/Au), to that reported for the oxygen-saturated surface (1.1 ML O/Au) [71]. This procedure leads to the formation of surface nanostructures (~2 nm diameter) [13,15,23,27]. Since the morphology (and oxidative chemistry) of the O/Au surface varies with the temperature chosen for  $O_3$ dosing [12,13], this temperature was set to 200 K. An <sup>18</sup>O/Au surface is prepared to perform isotopic labeling experiments by exposing the O/Au surface to 2 L of  $H_2^{18}$ O (1 L = 10<sup>-6</sup> Torr  $\cdot$  s) at 150 K and annealing to 220 K. By subsequently measuring the amount of <sup>16</sup>O<sub>2</sub>, <sup>16</sup>O<sup>18</sup>O and  $^{18}O_2$  (m/z = 32, 34 and 36, respectively) during the TPD of the oxygen covered surface, it was determined that ~80% of the surface oxygen is <sup>18</sup>0.

Benzyl alcohol (Sigma-Aldrich, 99.8%) was dosed at 150 K. While during condensation experiments doses sufficient to guarantee multilayer formation were employed, oxidation experiments were carried out using amounts corresponding to a saturated monolayer. However, when a second reactant was introduced (e.g. benzaldehyde, 99.5%; paraformaldehyde, 95%; methanol, 99.8%; all supplied by Sigma-Aldrich), a dose of benzyl alcohol sufficient to reach only half of a saturated monolayer of benzyl alcohol was employed. Compounds employed to react with benzyl alcohol were used in excess to favor the coupling reactions. An error of ~5% is estimated for the reported coverages of both benzyl alcohol and atomic O.

For TPRS experiments a heating rate of 5 K/s was employed. Reaction products were identified by comparing their cracking patterns to those of pure samples (Supporting Information, Table SI). The yield of each compound was quantified from the mass spectrometer intensity of its parent ion, which was corrected scaled by the ionization efficiency of the molecule, the relative intensity of the parent ion and instrumental (quadrupole transmission and multiplier gain) deviations [20,22]. Residual carbon after each experiment was quantified by exposing the surface to  $O_3$  and performing a TPRS experiment following oxidized carbon (as CO or  $CO_2$ ). Hereafter this procedure will be referred to as *post-oxidation TPRS*. Binding (adsorption) energies are estimated from desorption temperatures in TPRS data using the Redhead method [72], assuming in all cases a first-order reaction and a pre-exponential factor

of  $10^{15}$  [73–75]. The use of other factors (e.g.,  $10^{13}$ ) leads to a difference from the values reported here of about 10 kJ/mol.

# 3. Results and discussion

#### 3.1. The interaction of benzyl alcohol with clean Au(111)

Benzyl alcohol is relatively strongly bound to the gold surface, exhibiting binding energies of 90 and 105 kJ/mol, as deduced from a Redhead analysis of the desorption temperatures of a saturated layer (310 and 360 K, Fig. 1). Strong interactions between aromatic compounds and metal surfaces are common and are usually associated with adsorption geometries where the aromatic ring lies nearly parallel to the surface [76–82]. In the case of benzyl alcohol, analysis of the observed EELS vibrational modes according to the surface selection rules (Fig. 2 and Table 1) supports this binding geometry. While the multilayer of the alcohol features strong signals corresponding to modes whose dipole moments lay parallel to the ring (e.g.  $v_{C-0}$ ,  $v_{C-H}$ ), they are attenuated nearly ten-fold with respect to out-of-plane modes (e.g.  $\phi_{C-C}$  and  $\gamma_{C-H}$ ) at monolayer coverage [78]. The presence of two peaks is attributed to lateral, coverage dependent interactions in the adsorbed layer, but this effect was not studied in detail.

The strong interaction of benzyl alcohol with the gold surface apparently leads to thermal decomposition in the course of heating. Indeed, ~30% of the initial amount of adsorbed benzyl alcohol undergoes thermal decomposition on the gold surface, based on post-oxidation TPRS (Table 2). It is noteworthy that aliphatic alcohols have been shown to desorb cleanly from gold during temperature programmed desorption [9,11,18–20]. Thus, this fact indicates that benzyl alcohol can potentially poison a gold catalyst more easily than other alcohols, especially when high temperatures are employed [38].

#### 3.2. Quantitative analysis of the products of benzyl alcohol oxidation

As the initial amount of surface oxygen preadsorbed is increased, the overall reaction behavior shifts from partial oxidation toward combustion (Fig. 1). This dependence is quantitatively assessed in Table 2, where relative product yields (based on the total amount of product) are estimated from the corrected integrated intensities from TPRS experiments (the plotted data can be found in Fig. S1). Similarly to the behavior observed during condensation (Section 3.1), carbon deposition takes place during oxidation. This process is apparently inherent to the gold surface under the conditions of our experiments.

At lower oxygen precoverages partial oxidation to benzaldehyde and coupling to benzylbenzoate dominate the products. With higher oxygen precoverages benzoic acid and  $CO_2$  become the major products. High selectivities for partial oxidation are obtained at oxygen precoverages below 0.05 ML. Similarly, it has been reported that an increase in the concentration of oxidizing species under practical conditions (e.g. by increasing the amount of oxygen employed during the reaction) leads to a decrease in aldehyde selectivity [36,60,69]. These results are consistent with the inverse relationship between aldehyde selectivity and alcohol conversion observed in the liquid phase [29–32,35,45,59,69].

#### 3.3. Reaction mechanism during the oxidation of benzyl alcohol

Previous investigations using isotopically labeled alcohols have unequivocally demonstrated that the hydroxyl (OH) group is dehydrogenated; [9,83,84] accordingly, benzyl alcohol is expected to react with O to form benzyloxy ( $C_6H_5CH_2$ –O) species:

$$2C_6H_5 - CH_2 - OH + O \rightarrow 2C_6H_5CH_2 - O + H_2O.$$
 (1)

This facile dehydrogenation process yield water as a product near 200 K during TPRS experiments (Fig. 1). In addition, the initial



Fig. 1. Temperature-programmed desorption of benzyl alcohol and its oxidation products from a gold surface with various oxygen precoverages from 0.0 (i.e. desorption of BnOH from clean gold, bottom set of spectra) to 0.15 ML O (top set of spectra). In all cases the amount of alcohol adsorbed corresponds to that necessary to guarantee a saturated monolayer on clean Au.

changes in the HREEL spectra are consistent with this reaction (Fig. 2, Table 1). The characteristic  $\nu_{Au-O}$  on the oxygen-covered surface (360 cm<sup>-1</sup>) significantly decreases in intensity on exposure to benzyl alcohol at 140 K and disappears after heating to 190 K.

As the surface is annealed, benzyloxy species are further dehydrogenated. Between 190 and 240 K, the vibrational modes associated with the methylene (CH<sub>2</sub>) group in the alcohol,  $\nu_{C-H}$  at 2880 cm<sup>-1</sup> and  $\delta_{C-H}$  at



**Fig. 2.** Vibrational (HREEL) spectra of benzyl alcohol on clean and oxygen-covered gold surfaces. Benzyl alcohol multilayers were obtained by dosing the alcohol at 150 K; annealing to 230 K is sufficient to desorb the multilayers and leave a saturated monolayer. Oxidation experiments were carried out by adsorbing the alcohol on a 0.1 ML O/Au surface at 140 K, followed by annealing to the indicated temperatures.

1440 cm<sup>-1</sup>, have disappeared, consistent with benzaldehyde formation near this temperature:

$$2C_6H_5-CH_2-O+O \rightarrow 2C_6H_5CHO+H_2O.$$
 (2)

Together with the disappearance of the feature at 1440 cm<sup>-1</sup>, a weak feature emerges at 1360 cm<sup>-1</sup>, which is assigned to benzoate ( $\nu_{O-C-O}$ ) species, based on the formation of similar carboxylates during gold-mediated alcohol oxidation [9,11]. Corresponding to the removal of the aldehydic H atom to form benzoate, a second water feature appears in the TPRS spectra at 245 K when high O coverages are employed (Fig. 1). Indeed, TPRS of the oxidation of benzaldehyde shows that water evolves at 240 K (Fig. S2), indicating that benzoate formation occurs as follows:

$$2C_6H_5-CHO + 3O \rightarrow 2C_6H_5COO + H_2O.$$
(3)

Based on previous studies [11,13], reaction (3) can be explained as the consequence of two reactions:

$$C_6H_5-CHO + O \rightarrow C_6H_5CHOO$$
(3a)

$$2C_6H_5-CHOO + O \rightarrow C_6H_5COO + H_2O.$$
 (3b)

Benzoic acid evolves at 350 K without  $CO_2$  evolution at an oxygen coverage of 0.08 ML. This minor pathway is restricted to a narrow span of O coverages, and we suggest it occurs when the oxygen concentration is sufficient to promote the formation of C<sub>6</sub>H<sub>5</sub>CHOO (Eq. (3a)) but not that of benzoate (Eq. (3b)), and that C<sub>6</sub>H<sub>5</sub>CHOO rearranges at 350 K to yield benzoic acid.

In agreement with Eq. (3), HREELS experiments following the oxidation of benzaldehyde show the formation of the  $\nu_{O-C-O}$  mode upon annealing to temperatures as low as 300 K (Fig. S3). It is then clear that benzoate species are surface products of benzaldehyde oxidation, which later evolve as benzoic acid and CO<sub>2</sub>:

$$2C_6H_5$$
-COO $\rightarrow$ C $_6H_5$ COOH + CO $_2$  + residual carbon. (4)

(Neither steps 3b or 4 are considered to be elementary steps, but the others are.)

This reaction was confirmed by performing oxidations with <sup>18</sup>O and following the labeled products by TPRS (Fig. 3). Both benzoic acid and  $CO_2$  incorporate <sup>18</sup>O atoms in their structure and the ratio of <sup>18</sup>O/<sup>16</sup>O in the products is the same in both cases, which strongly suggest that benzoic acid and  $CO_2$  are formed through the benzoate intermediate.

Oxidation with <sup>18</sup>O show that benzyl benzoate does not incorporate <sup>18</sup>O into its structure, as evidenced from the absence of m/z = 214 and

# Table 1

Assigned vibration <sup>a</sup>	Multilayer on clean Au	Monolayer on clean Au	Monolayer on O/Au, 140 K	Monolayer on O/Au, 240 K	Monolayer on O/Au, 300 K	Monolayer on O/Au, 400 K	References
$\phi(C-C)_{o}$	420	420	420	420	420	420	[74]
$\gamma$ (C–H) <sub>o</sub>	720	720	720	720	720	700	[74]
$\nu$ (C-O) <sub>i</sub>	1020	1020	1020	-	-	-	[9,18]
$v(0-C-0)_i$	-	-	-	-	1360	1360	[9,18]
$\delta(CH_2)_o$	1440	1440	1440	1440	-	-	[18]
$\nu$ (C–H) <sub>o methylene</sub>	2850	2840	2840	-	-	-	[18]
$\nu$ (C–H) <sub>i ring</sub>	3010	3010	3010	3010	3020	3020	[74]

Selected electron energy losses during the condensation/oxidation of benzyl alcohol on Au(111). The assignment has been based on the indicated references.

Depending on the orientation of the dipole moment with respect to the aromatic ring, vibrational modes are catalogued as in-plane or out-of-plane by subscripts i and o, respectively.

)

m/z = 216 (Fig. 3). This result indicates that the ester is not formed through benzoate or benzoic acid. Instead, benzyl benzoate is formed through the coupling of two unlabeled species. Following the pathway elucidated for lower molecular weight alcohols [9,11], this coupling reaction is

$$C_6H_5$$
-CH<sub>2</sub>-O +  $C_6H_5$ -CHO +  $^{1}/_2O$ → $C_6H_5CH_2$ -O-C(O)- $C_6H_5$   
+  $^{1}/_2H_2O$  (5)

which is comprised of the following elementary steps:

$$C_6H_5-CH_2-O+C_6H_5-CHO \rightarrow C_6H_5CH_2-O-CH(=O)-C_6H_5$$
 (5a)

$$C_6H_5CH_2$$
-O-CH-O- $C_6H_5$  + O $\rightarrow$   $C_6H_5CH_2$ -O-C(O)- $C_6H_5$  + OH (5b)

 $2OH \rightarrow O + H_2O.$ (5c)

Ester formation can be viewed as the result of the nucleophilic attack of benzyloxy species onto a benzaldehyde molecule to form the hemiacetal (Eq. (5a)), which  $\beta$ -hydride eliminates to liberate the ester (Eq. (5b)).

When benzaldehyde was added to a benzyloxy-covered surface [19], obtained by exposure of an oxygen-covered surface to benzyl alcohol at 150 K, the amount of benzyl benzoate produced doubled, confirming reaction (5) (Fig. S4). Similarly, the addition of formaldehyde to the benzyloxy-covered surface resulted in the formation of benzyl formate (Fig. S4), following the coupling reaction shown in Scheme 1 (a). These results suggest the synthesis of targeted benzyl esters by introducing any aldehyde into the reactor during benzyl alcohol oxidation.

#### 3.4. Kinetics of benzyl alcohol oxidation

In order to determine the temperature at which the benzyloxy dehydrogenates to benzaldehyde and subsequent reaction occurs to form the ester (Eq. (5)), surfaces pre-covered with 0.05 ML of O were dosed with benzyl alcohol at 150 K and flash-annealed to increasingly higher temperatures. Subsequent dosing with formaldehyde was then done to probe for unreacted benzyloxy species by following benzyl formate formation (Scheme 1 (a)) by TPRS (Fig. 4).

Pre-annealing temperatures below 170 K result in low yields for benzaldehyde and benzyl benzoate and in significant amounts of benzyl formate. However, at higher temperatures benzaldehyde and benzyl benzoate are produced in higher yields, clearly indicating that they are formed prior to the introduction of formaldehyde. The yield of benzyl formate progressively decreases and is negligible upon annealing above 220 K (data not shown). From the inflexion points of the sigmoidal curves in Fig. 5, we determine that the formation of benzaldehyde and benzyl benzoate takes place at 175 K and 185 K, respectively. This temperature is approximately 65 K below the formation of benzoate species, corresponding to a difference of 20 kJ/mol in the kinetic barriers (~50 kJ/mol for aldehyde/ester formation, ~70 kJ/mol for benzoate formation). This difference in kinetic barriers is rather significant, especially when compared to other alcohols. For example, the gold-mediated oxidation of methanol, previously investigated in our group, indicates that the corresponding aldehyde and ester (formaldehyde and methyl formate) are produced at 220 K, temperature very close to that at which formate (precursor to formic acid) is observed spectroscopically (225 K). Thus, compared to methanol (and, presumably, to other aliphatic alcohols), benzyl alcohol can be selectively oxidized to benzaldehyde/benzyl benzoate due to the fact that further oxidation is kinetically hindered.

Since the formation of aldehyde/ester requires lower temperatures for benzyl alcohol (175 K) than for methanol (220 K), it would be expected that the oxidation of a mixture of these two alcohols will lead mostly to coupling of benzaldehyde with methoxy and benzyloxy (benzyl- and methyl- benzoate), in detriment of those involving the formation of formaldehyde (methyl- and benzyl- formate), as shown in Scheme 1a and b. Indeed, the coupling products detected from the oxidation of these mixtures are exclusively benzoates (Table 3 and Fig. S5), regardless of the order in which these alcohols are dosed. The formation of methyl formate observed when only methanol is dosed is completely suppressed in the presence of benzyl alcohol. Conversely, the formation of benzyl benzoate is not affected by the presence of methanol. The only cross-coupling product detected is methyl benzoate (although both benzyl formate and methyl benzoate feature a parent ion m/z = 136, they can be distinguished by their different desorption temperatures, as shown in Fig. S5). Thus, the formation of formaldehyde and its coupling products is intercepted by the formation of benzaldehyde and its coupling products, benzoate esters. This preference has been previously seen under working conditions [43,52,70], providing further support to the applicability of our mechanism to vastly different reaction conditions.

#### Table 2

Relative yields during the oxidation of benzyl alcohol on a gold surface covered with various amounts of oxygen. Mass spectrometer integrated areas have been quantified according to the procedures described in Section 2.

O coverage (ML)	Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl benzoate	Combustion gases $(CO + CO_2)$	Residual carbon
0.00	73	0	0	0	0	27
0.02	54	7	0	2	0	37
0.05	38	15	1	6	0	40
0.08	20	18	2	6	13	41
0.12	0	5	1	1	46	47
0.15	0	4	2	0	65	29



**Fig. 3.** Temperature-programmed desorption of selected oxidation products from the Au surface covered with a mixture of <sup>18</sup>O and <sup>16</sup>O at two different coverages. The insertion of one and two <sup>18</sup>O in the resulting products is represented with one and two asterisks, respectively.



**Fig. 4.** Yield (MS integrated intensities) of selected oxidation products from the benzyloxy/formaldehyde coupling as a function of the pre-annealing temperature of benzyloxy/Au prior to formaldehyde dosing. Reactions are performed on a 0.03 ML O/Au surface to ensure that only benzaldehyde and the corresponding esters are formed.



**Scheme 1.** Esters formed through the coupling of a) benzyl alcohol and formaldehyde, b) methanol and benzaldehyde, and c) methanol and formaldehyde.

## Table 3

Relative integrated intensities of characteristic traces associated with the gold-mediated coupling of methanol, benzyl alcohol, and a mixture of them. In the latter case, two sequences for dosing were considered. Alcohols were dosed at 150 K on a 0.05 ML O/Au surface, using doses close to ½ saturated monolayer.

Substrates	(m/z=60) Methyl formate	(m/z=212) Benzyl benzoate	(m/z=136) Methyl benzoate
Methanol	100	0	0
1st methanol	0	100	60
2nd benzyl alcohol			
1st benzyl alcohol	0	100	100
2nd methanol			
Benzyl alcohol	0	100	0

# 4. Conclusions

The remarkable selectivity achieved during the gold-mediated oxidation of benzyl alcohol is associated with conditions in which benzyl alcohol is in excess with respect to surface atomic oxygen. The kinetic barrier for aldehyde formation is found to be ~20 kJ/mol lower than that for benzoate formation (which ultimately leads to benzoic acid and combustion gases). This difference is sufficiently large to ensure a selective oxidation to benzaldehyde.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10. 1016/j.susc.2012.03.013.

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