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Selective Oxidation of Styrene on an Oxygen-Covered Au(111)

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There is considerable interest in the reactivity of gold[1−5] since the discovery that Au nanoclusters supported on reducible metal oxides are highly active for CO[6,7] and propene oxidation[6,8] at low temperature. The selective epoxidation of propene is an extremely important industrial process that has potential for many synthetic applications. The reason for the high activity of supported Au nanoparticles is a subject of active debate. One view is that the small size of these particles imparts unique chemical properties to the Au not found in bulk gold.[1,9] Another explanation is a synergetic interaction, that is, the partial electron transfer, between the gold and the metal oxide support.[10] To test the idea, we have undertaken a series of studies to determine the activity of the extended Au-(111) single-crystal surface. Indeed, for the first time, we are able to promote the *selective* oxidation of olefins on single-crystal Au covered with oxygen atoms, which demonstrates that extended Au is an effective material for olefin oxidation.

One obstacle to oxidation of olefins on Au is the difficulty of dissociating O_2. Indeed, it is likely that O_2 dissociation is rate-controlling under some conditions.[11−13] Nevertheless, elementary steps important in olefin oxidation can be studied by depositing oxygen on the Au surface using other means. The preoxidation of metal surfaces in order to study oxidation reactions is a widely used approach that has offered insight into important processes, including CO and olefin oxidation.[4,14,15] We devised a method for depositing oxygen atoms on Au by electron bombardment of condensed NO_2 that allows us to control the oxygen coverage up to a maximum coverage of 0.4 ML.[16] In this study, we fix the oxygen coverage at 0.2 ML. The deposition of oxygen onto the Au(111) surface changes its structure and releases Au atoms from the surface; however, the surface maintains a smooth morphology.[17] Oxygen deposited using this method is relatively strongly bound to the Au(111) surface, desorbing as O_2 at ∼550 K.[16]

In this communication, we report on the selective oxidation of styrene by O-covered Au(111). Styrene was used because it is analogous in reactivity to ethylene, but has a higher molecular weight and, therefore, a relatively high desorption temperature. Thus, the surface residence time of the olefin is increased at the temperature necessary for oxidation of the hydrocarbon. A recent NEXAFS study has determined the similar adsorption geometries of styrene, propene, and ethylene on Ag(111),[18] validating the use of styrene as a model terminal alkene for the investigation of olefin epoxidation study.

Styrene (Alfa Aesar, 99.5%) was selectively oxidized to styrene epoxide, benzoic acid, and benzeneacetic acid during temperature-programmed reaction (TPRS) of styrene on 0.2 ML chemisorbed oxygen covered Au(111) (Figure 1). Specifically, styrene epoxide ($m/z = 120$, parent ion) is evolved in a peak at 350 K. The organic acid products are formed at somewhat higher temperatures: benzoic acid (C_6H_5COOH, $m/z = 122$, parent ion) is observed in a broad
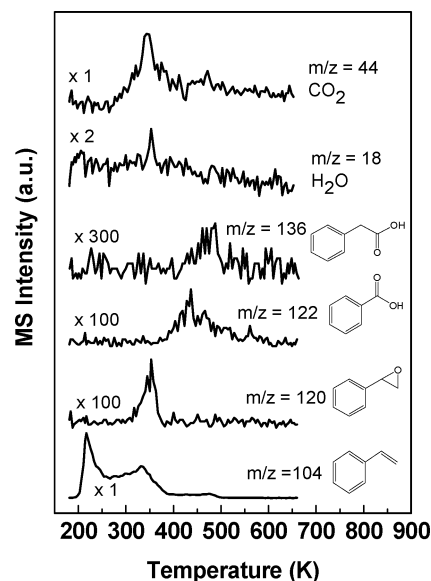
Figure 1. Temperature-programmed reaction of styrene on 0.2 ML chemisorbed oxygen-covered Au(111). The average heating rate was ∼10 K/s. The styrene adsorption temperature was 130 K, and multiple layers were adsorbed initially.

peak centered at 440 K, and benzeneacetic acid ($C_6H_5CH_2COOH$, $m/z = 136$, parent ion) is detected at 480 K. No benzene formation is detected. The absence of a $m/z = 29$ peak in our data rules out other possible oxygenated products, including formaldehyde.

Styrene epoxide was unequivocally identified by quantitative comparison of the fragmentation pattern of the product to those measured for other geometric isomers, that is, benzeneacetaldehyde ($m/z = 120$, parent ion) and acetophenone ($m/z = 120$, parent ion). Specifically, the presence of $m/z = 119$ and 91 fragmentation patterns (1:3 intensity ratio) associated with the parent ion peak confirms the formation of styrene epoxide and rules out the other two geometric isomers. Similarly, benzoic acid and benzeneacetic acid have been identified based on their corresponding fragmentation patterns, in addition to the parent ions.

Combustion products, such as H_2O and CO_2, were also produced in a peak at 350 K (Figure 1). The CO_2 is produced either from combustion of styrene itself or oxidation of the CH_2 group released in conjunction with formation of benzoic acid. No residual O_2 is evolved from the surface during temperature-programmed reaction, which indicates a high overall activity since all adsorbed oxygen was consumed during the oxidation of styrene (data not shown). Some styrene ($m/z = 104$, parent ion) molecularly desorbs at 220 K (multilayer) and 330 K (monolayer). Small amount of residual carbon was detected on the surface after reaction.

The selectivity for formation of styrene epoxide is ∼53%, as estimated by quantitative analysis of our temperature-programmed reaction data (see Supporting Information). Combustion to CO_2
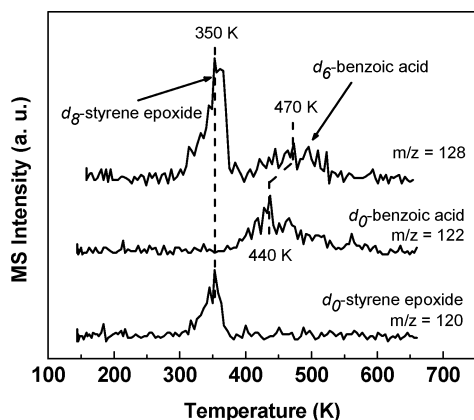
Figure 2. Temperature-programmed reaction of d_0-styrene and d_8-styrene on 0.2 ML oxygen-covered Au(111). The average heating rate was ∼10 K/s. The styrene adsorption temperature was 130 K.
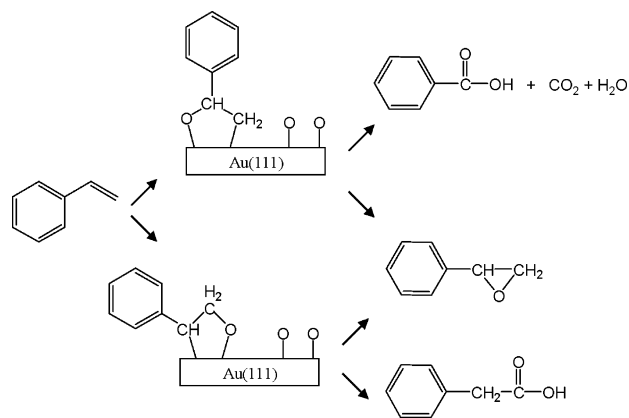

Figure 3. Proposed scheme for styrene oxidation on O-covered Au(111).

accounts for ∼20% of the styrene reaction. The remaining styrene forms benzoic acid (∼20%) and benzeneacetic acid (∼7%).

Investigation of deuterated d_8-styrene provides evidence that there is no C−H(D) bond activation in the rate-limiting step for epoxide formation, but that C−H(D) bond breaking is important in determining the rate of formation of both acids (Figure 2). The temperature for d_8-styrene epoxide ($m/z = 128$, parent ion) evolution was 350 K, the same as for the d_0-isomer. On the other hand, the peak temperatures are 30 K higher for both deuterated benzoic acid ($m/z = 128$, parent ion) and deuterated benzeneacetic acid ($m/z = 98$, the most intense fragmentation) compared to their undeuterated counterparts. In addition to the temperature shift, the yield of epoxide relative to the acids was increased for the reaction of d_8-styrene. Specifically, the ratios of parent ions for the epoxide and benzoic acid were 0.9:1 and 2:1 for using d_0-styrene and d_8-styrene, respectively.

Vibrational (high-resolution electron energy loss) spectroscopy indicates that the phenyl ring remains intact up to 350 K, and that no benzoate or other analogous species are formed during styrene oxidation (Figure S1). Benzoate or other analogous species would be signified by intense vibrational peaks associated with the O−C−O symmetric stretch at ∼1420 cm^{-1} based on analogy with studies of Cu;[19] however, none were detected in spectra collected after heating to 130, 250, 300, or 350 K. The persistence of the ring is indicated by the presence of the C−H stretch mode at 3060 cm^{-1} and a mode associated with the phenyl ring at 710 cm^{-1} tentatively assigned to the γ(C−H) mode.

On the basis of our data and comparison with the literature for related systems, such as Ag, we propose that styrene oxidation proceeds via an oxametallacycle intermediate.[20,21] Earlier studies[22,23] also addressed the issue of a common intermediate for both selective and nonselective channels in ethylene epoxidation. Considering the asymmetry of styrene C=C bond, a reaction scheme involving oxametallacycle intermediates for the styrene oxidation on Au(111) is proposed in Figure 3.

In conclusion, we have shown that oxidation of styrene on chemisorbed oxygen covered Au(111) selectively yields styrene oxide, benzoic acid, and benzeneacetic acid. Most styrene is selectively oxidized with only ∼20% completely combusting. This work illustrates that extended Au surfaces are capable of promoting selective hydrocarbon oxidation once the oxygen atoms are seeded on the surface. Thus, the seemingly unique oxidation activity of supported Au nanoparticles is most likely primarily due to their ability to dissociate O_2. On the basis of our earlier work, undercoordinated Au atoms, even on an extended Au surface and without a metal oxide support, can induce O_2 dissociation.[16] While support interactions and quantum-size effects may modify the reactivity of Au, metallic Au itself is capable of promoting selective olefin oxidation.

Supporting Information Available: Details for the Experimental Section, selectivity estimation, and styrene vibrational mode assignments. This material is available free of charge via the Internet at http://pubs.acs.org.

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