Long-range ordering of stable, surface-bound intermediates: RAIRS, TPRS and STM studies of toluene oxidation on Ag(110)

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ABSTRACT

There is long-term interest in catalyst poisoning due to the buildup of carbonaceous species on catalytic metal surfaces. These species are often derived from the reactants themselves in reactions parallel to the primary catalytic cycle. Generally, these species are believed to be randomly distributed on the surface, with locally high concentrations. Using scanning tunneling microscopy (STM), we have found that upon annealing to 400 K a stable intermediate formed by partial oxidation of toluene on Ag(110) forms highly ordered domains with a length scale well over 1000 Å, limited only by the size of surface terraces. Temperature-programmed reaction spectroscopy and STM suggest the intermediate to be adsorbed benzoate species, C₆H₅CHOO, which decomposes to carbon dioxide and benzene near 550 K when heated.

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1. Introduction

There has been great interest in understanding the ordering of organic monolayers for because of their role as catalyst poisons, as well as for their applicability to optoelectronic applications [1,2]. Ordering over large length scales can improve the properties of polymeric materials, such as their conductivity and mechanical stability, by orders-of-magnitude compared to those of randomly distributed materials [3]. However, complex molecular adsorbates on reactive surfaces generally show ordering only over a limited length scale [4]. For example, typical ordered domain sizes for self-assembled monolayers of alkanethiols are in the range of only 80–120 Å [5]. Here, we find with scanning tunneling microscopy (STM) that the reactive surface
intermediate resulting from the partial oxidation of toluene by adsorbed atomic oxygen on Ag(110) self-organizes into ordered domains larger than 1000 Å, limited only by the size of the terrace.

Partial oxidation of toluene is an industrially important process, yielding products such as benzyl alcohol [6, 7], benzaldehyde [8–10] and benzoic acid [11] over various catalysts, in all of which silver is an essential ingredient. However, it is not understood why silver is needed in these catalysts. No detailed studies of the structural aspects of toluene oxidation on a silver surface have been carried out previously to the best of our knowledge. Using temperature-programmed reaction spectroscopy (TPRS), we have investigated the reactions of toluene with adsorbed atomic oxygen on Ag(110).

2. Experimental

The experiments were performed in ultrahigh vacuum (UHV) chambers equipped with STM (SPM 100, RHK), low energy electron diffraction (LEED), Auger electron spectroscopy (AES) (PRI 179), a quadrupole mass spectrometer (QME 200, Balzers) and reflection-absorption infrared spectroscopy (RAIRS). Sample cleaning and LEED/AES were carried out in a preparation chamber (typical base pressure ~ 2 × 10⁻¹⁰ Torr) directly connected to the STM chamber (typical base pressure ~ 4 × 10⁻¹⁰ Torr). Sample transfer between the two chambers took approximately 2 min. The Pt/Ir tip used for STM was prepared using field evaporation in vacuum onto a gold single crystal (~ 4 μA, 15 min). Scan dimensions were calibrated using the p(2 × 1) oxygen structure on Ag(110). STM measurements were made at 300 K. All images were processed with x-offset and x-slope subtraction; some were smoothed. TPRS measurements were carried out in a separate UHV chamber equipped with a UTI 100C quadrupole mass spectrometer. A glass cap with a 3 mm orifice was mounted over the ionizer to limit detection to species desorbing from the front face of the crystal. A linear heating rate of 2 K/s was used in the TPRS measurements. The IR spectra were obtained with a Nicolet Nexus 470 Fourier transform infrared spectrometer with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector. Sample and background spectra (with the crystal at constant temperature) were collected by averaging 1000 scans at 4 cm⁻¹ resolution over an acquisition time of 10 min.

The Ag(110) crystal was aligned to within 0.5° of the (110) plane using Laue backscattering and was mechanically polished down to 0.25 μm diamond paste. The surface was cleaned by cycles of Ar ion bombardment (2 μA, 500 eV, 15 min at 300 K), oxygen treatment (1 × 10⁻⁶ Torr at 500 K, 15 min) and annealing at 800 K (5 min). Final cleaning was achieved using oxygen adsorption–desorption cycles (1 × 10⁻⁶ Torr for 15 min at 300 K and flashing the sample to 800 K) until no CO or CO₂ desorbed from the surface. After the oxygen cleaning, the chamber pressure usually increased to 2 × 10⁻⁹ Torr, with the major background gases being H₂, H₂O, CO and CO₂. STM images showed that the clean Ag(110) surface was comprised of both large (several thousand angstroms wide) and small terraces.

The purity of toluene (d₀, Aldrich, 99.8%) and O₂ (g) (Praxair, 99.999%) was verified by mass spectrometry during dosing. Isotopically labeled (d₀ and d₁) were used with no further purification. Isotopic purities were 99% (d₀) and 98% (d₁), respectively. Oxygen was delivered to the surface via a capillary array doser and toluene via a needle doser. All exposures are reported in units of Langmuir (1 L = 10⁻⁶ Torr s) using background pressure.

3. Results and discussion

3.1. Reflection-absorption infrared spectroscopy

RAIRS measurements were used to elucidate the nature of the reactive intermediate on the surfaces Figure 1(b). IR bands observed following toluene exposure to Ag(110)-p(2x1)-O and Ag(110)-p(2x1)-¹⁸O (Figure 1(a)) and their corresponding assignments are summarized in Table 1. The IR measurements were made at 330 K to limit contribution from molecularly adsorbed toluene (see next section). The spectra suggest the formation of a benzoate-type surface intermediate with the plane of the molecule normal to the surface. The vibrational features observed at 1410 and 719 cm⁻¹ following toluene adsorption on Ag(110)-p(2x1)-O at room temperature are ascribed to the carboxylate symmetric stretch, ν_s(OCO), and deformation, δ(OCO), which are in agreement with those for benzoate on Cu(110) [12]. The ν_s(OCO) assignment is consistent with the observed red-
shifting of the band at 1410–1338 cm\(^{-1}\) following toluene adsorption on Ag(110)-p(2x1).\(^{18}\)O. The bands at 3021 and 3018 cm\(^{-1}\) are due to C-H stretches associated with the C\(_6\)H\(_5\) ring. The peak at 2966 cm\(^{-1}\), which does not shift significantly after toluene adsorption on Ag(110)-p(2x1).\(^{18}\)O, is attributed to a C-H stretching mode of the methyl carbon associated with some unoxidized adsorbed C\(_6\)H\(_6\)CH\(_3\) species.\(^{13}\) Redistribution of the intensities and frequencies of the vibrational peaks below 1450 cm\(^{-1}\) with O\(^{18}\) substitution are attributed to mode coupling. Temperature programmed reaction experiments\(^{14}\) with isotopically labeled toluene suggests that only the methyl hydrogen is removed by reaction with adsorbed oxygen atoms in formation of the intermediate (see below). Overall, the vibrational peak assignments are consistent with the formation of adsorbed C\(_6\)H\(_5\)COO following toluene adsorption on Ag(110)-p(2x1)-O.

### 3.2. Temperature-programmed reaction spectroscopy

Oxygen was first dissociated on the clean C\(_6\)H\(_5\)COO(a) \(\rightarrow\) C\(_6\)H\(_5\)(g) + CO\(_2\)(g) + C(a) Ag(110) surface to form atomicallyadsorbed oxygen at prescribed coverages. The surface was then cooled to 125 K, exposed to 3 L of toluene and heated. The only volatile products detected were molecular toluene (C\(_6\)H\(_6\)CH\(_3\), ≤320 K), water (H\(_2\)O, 300 K), carbon dioxide (CO\(_2\), 575 K) and benzene (C\(_6\)H\(_6\), 575 K) (Figure 2). No dioxygen desorbed. A significant amount of surface carbon was detected by AES after the TPRS measurements. Similar experiments with C\(_6\)D\(_5\)CH\(_3\) showed the hydrogens in water to originate from the methyl group, whereas those in benzene originate from the ring. Since molecularly adsorbed CO\(_2\) or benzene on Ag(110) desorbs below 300 K,\(^{15}\) the simultaneous evolution of CO\(_2\) and benzene peaks at 575 K (Figure 2) indicates a common single rate-limiting step for their origin. The peaks for CO\(_2\) and benzene are compared for several initial oxygen coverages in Figure 2. In all cases, CO\(_2\) and benzene exhibit the same peak temperature and the same peak shape. Furthermore, the ratio of their peak areas (uncorrected for sensitivity factors) remains constant at 4.2. These observations support the assertion that CO\(_2\) and benzene originate from a common intermediate. The fact that no H\(_2\) or H\(_2\)O evolves from C\(_6\)H\(_5\)CH\(_3\) above 350 K and that no H is found in benzene from C\(_6\)D\(_5\)CH\(_3\) suggests that the hydrogen atoms on the methyl group of toluene react to form H\(_2\)O(g) below this temperature. The identification of C\(_6\)H\(_5\)CHO as further consistent with the fact that there are no free oxygen atoms left on the surface (see also STM results below) following reaction between toluene and Ag(110)-p(2x1)-O.

The net reaction below 500 K is thus concluded to be:

\[
C_6H_5CH_3 + 3O(a) \rightarrow C_6H_5COO(a) + 3/2H_2O(g)
\]

At 500–600 K:

\[
C_6H_5COO(a) \rightarrow C_6H_5(g) + CO_2(g) + C(a)
\]

Activation of the methyl hydrogens in toluene by adsorbed O is expected from the relatively high gas phase acidity of toluene and the well-established Bronsted basicity of adsorbed atomic oxygen on metallic silver.\(^{16}\) Apparently adsorbed oxygen atoms then readily attach to the denuded carbon atom.

### 3.3. Scanning tunneling microscopy at 300 K

Based on the TPRS measurements described above (Figure 2), at a surface temperature of 300 K hydroxyl, the benzoate may be present on the surface, and
scanning tunneling microscopy was used to probe its spatial distribution. In the STM experiments, the initial atomic oxygen coverage was 0.45 ML. The oxygen-covered Ag(110) surface was exposed to 7 L toluene at 300 K. Thereafter, STM imaging was performed also at 300 K. No remnants of p(2x1)O were observed.

Two types of ordered structures, however, were clearly visible (Figure 3(a,b)). The c(4 × 2) structure in Figure 3(c) resembles that of close-packed monolayer benzene on Ag(110) at 4 K [17] and that of phenoxy on Cu(110) at 300 K [18]. Utilizing the results of the vibrational spectra obtained after annealing to 330 K, we assign this structure to the benzoate intermediate. The features inside the benzoate domains (e.g. circled in Figure 3(a,b)) are point vacancies. The p(2 × 2) string structure shown in Figure 3(d) is similar to that observed for OH(a) on Ag (110) [19] and is assigned to hydroxyl, which is expected to persist at room temperature after the reaction between toluene and adsorbed O. These assignments are supported by the images observed after annealing to 400 K (see next section), where the hydroxyl structure disappears and the benzoate structure remains. Clean surface regions were also seen (Figure 3(a,b,d)), and the clean Ag (110)-(1 × 1) rows along the <1ī0> axis were resolved (Figure 3(d)). A small amount of molecularly adsorbed toluene may exist on the clean regions, but may be too mobile to be imaged at 300 K. From the large-scale images in Figure 3(a,b), the size of the ordered domains of benzoate is estimated to be from 200 to 700 Å. The length of the hydroxyl strings is up to 400 Å. The hydroxyl structures seem to always appear at the boundaries of the benzoate domains, and thus may be limit their size.

The limitation of benzoate domain size by the hydroxyl structures is demonstrated by sequential imaging of the boxed region in Figure 3(b). Figure 4 displays selected frames from an STM movie recorded at about 35 s per frame. Free hydroxyl structures (marked by an arrow in frame 16) appear to be mobile from frames 16 to 19 if they do not border benzoate domains. However, when both ends of such a string are connected to benzoate domains (marked by an arrow in frame 46), the hydroxyl string becomes immobile (frame 46 to 49). On the other hand, the boundaries of the benzoate domains fluctuate significantly (from 38 to 42), indicating that benzoate intermediates near the domain boundaries are mobile when they are not pinned by hydroxyl strings. The mobility does not seem to be caused by the scanning STM tip as it is independent of scanning directions. These observations suggest that if the immobile hydroxyl strings were removed, the benzoate domains would grow in size. This is confirmed by the annealing experiments described in the next section.

Figure 3. Scanning tunneling microscopic images for reaction intermediates in toluene oxidation at 300 K. (a) and (b) Overlaid STM images of a continuous long stripe in a large-scale. (c) and (d) Details of two types of order structures. The initial atomic oxygen coverage was 0.45 ML. The oxygen-covered Ag(110) surface was exposed to 7 L toluene at 300 K. The boxed region in (b) was monitored versus time in Figure 4.
3.4. Scanning tunneling microscopy following heating to 400 K

Further experiments were carried out in order to isolate and image the benzoate intermediates. According to the TPRS measurements (Figure 2), all hydroxyl species have left the surface as water by 400 K, while the benzoate intermediate remains stable. Thus, for these STM experiments, the oxygen-covered (0.45 ML) Ag(110) surface was exposed to 15 L toluene at 300 K, then heated to 400 K and cooled to 300 K where imaging was performed. The same c(4 × 2) benzoate structures are seen everywhere in the images (Figure 5). As expected, the hydroxyl strings are absent. The size of ordered benzoate domains is well over 1000 Å on the large terrace – much larger than those observed without annealing (cf. Figure 3). The increased domain size appears to be due to the increased mobility of benzoate at higher temperature and to the elimination of hydroxyl species from the boundaries. In fact, except for a few point defects, no domain boundaries in the benzoate structure are observed (Figure 5). The benzoate domain size appears to be solely limited by the size of the terrace – a single domain on each terrace (right side of Figure 5(b)).

Closer inspection by STM over a larger length scale, however, does reveal some imperfections inside a single large domain (Figure 6(a)). The boxed terrace region is magnified in the overlaid STM images in Figure 6(b). Close inspection reveals two types of regions (marked A and B) that display different contrast (or corrugation). The contrast was observed to switch between A and B (Figure 6(c)). Such a switch may be caused by changes in the composition or shape of the STM tip, or by domains of different structure since the tunneling conditions were the same. The former is unlikely as the boundary is not perpendicular to the scan direction. A high-resolution STM image (Figure 6(d)) shows the details of the two different regions, and suggests that local defects in the 2D structure may lead to the A and B domains observed. Further, benzoate intermediates in the two regions appear to sit at the same lattice registry; there is no shift in binding sites, and both have the same c (4 × 2) periodicity. Therefore, the differences in contrast in the STM image are not likely to be caused by different binding sites or by different orientation of the benzyl ring (flat-lying, tilt or standing-up). On the other hand, different orientation of the carboxylate group on the benzoate intermediates may produce the effect. In fact, two possible orientations that differ by 180° with respect to the <110> axis are entirely equivalent, in a similar manner to that observed for phenoxy on Cu(110) [17].
4. Summary

The oxidation of toluene by atomic oxygen on the Ag (110) surface has been studied with RAIRS, TPRS and STM. The results are summarized as follows:

(1) RAIRS measurements are suggestive of a benzoate-type surface intermediate, namely C₆H₅COO. This intermediate is created by specific reaction of toluene with adsorbed...
atomic oxygen, which is the source of the catalytic activity of silver for toluene oxidation.

(2) The only volatile products are molecularly adsorbed toluene (C₈H₈, ≤320 K), water (H₂O, 300 K), carbon dioxide (CO₂, 575 K) and benzene (C₆H₆, 575 K).

(3) The concurrent evolution of CO₂ and C₆H₆ with the same peak temperature and peak shape, and constant ratio of peak areas at various initial oxygen coverages, are consistent with a C₆H₆CHOO surface intermediate.

(4) Below 350 K, all hydrogen atoms on the methyl group of toluene either react with oxygen to form water or remain associated with the carboxylate carbon. No free oxygen atoms are left on the surface to form water above 350 K. All remaining oxygen atoms are bonded to the intermediate.

(5) The benzoate-type intermediate forms a c(4 × 2) structure. Hydroxyl species form a p(2 × 2) string structure at 300 K.

(6) The size of ordered benzoate domains ranges from 200 to 700 Å at 300 K due to limitation by immobile hydroxyl strings. The benzoate intermediates near the domain boundaries are mobile at 300 K.

(7) Heating the surface to 400 K to eliminate hydroxyl species increases the size of ordered benzoate domains to over 1000 Å, limited only by the terrace size.

(8) Two equivalent orientations of the carboxylate group on the benzoate intermediates may produce domains of different orientations within the ordered benzoate domains.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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