Cesium Promotion in Styrene Epoxidation on Silver Catalysts

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The epoxidation of alkenes is of significant chemical importance.[1] In some cases it is heterogeneously catalyzed by silver particles with a size distribution from 0.1 to 10 μm supported on α-alumina.[2] Though the catalytic production of ethylene oxide[3,4] dominates industrial applications, epoxidation of alkenes with higher molecular weight has received increasing attention.[5] Supported silver particles primarily expose the (111) facet as a result of its energetic stability, but minor amounts of the less stable (100) and (110) surfaces are also exposed. The distribution of surfaces may affect the reaction selectivity. Cesium and a plethora of oxyanions are added to achieve high selectivity for epoxidation of ethylene,[3,4,6] butadiene,[7] and styrene.[8] The origin of the promotional effect of cesium has been widely debated and remains unresolved.[7−13]

In this communication, we report that low concentrations of Cs adsorbed on Ag(110) cause a structural change that provides a chemical switch for the epoxidation of styrene, completely reversing the preferred partial oxidation product from phenylacetaldehyde to styrene oxide. Styrene epoxidation is structure-sensitive on silver. In contrast to a strong preference for the formation of styrene oxide on Ag(111), phenylacetaldehyde (and phenylketene) dominate as the partial oxidation products on Ag(110) (Figure S1 in the Supporting Information).[14,15] In this study, we show scanning tunneling microscopy (STM) evidence of a structural modification induced by small amounts of cesium in which the Ag(110) surface reconstructs to form (111) microfacets, causing it to react much like the (111) surface for styrene oxidation.

The oxidation products on Ag(111) include styrene oxide along with the combustion products CO_2 and H_2O and minor secondary oxidation products benzoic acid, benzeneacetic acid, phenyl, biphenyl, and benzene.[16] On Ag(110), however, only a very small amount of styrene oxide forms; instead, phenylacetaldehyde and phenylketene dominate the partial oxidation, while the secondary oxidation products remain the same.[15] When as little as 0.1 monolayer (ML) of Cs is preadsorbed on the Ag(110) surface, the dominant partial oxidation product of styrene switches to styrene oxide (Figure 1), produced at the same low temperature as on Ag(111).[15] The secondary oxidation products (benzoic acid, benzeneacetic acid, phenyl, biphenyl, and benzene) are also partially suppressed by the Cs. The suppression of the secondary products was also observed in the oxidation of styrene on 0.1 ML Cs-covered Ag(111), without significant effect on the amount of epoxidation (Figure S2). This is in agreement with earlier works.[9,11] Obviously, the addition of cesium switches the selectivity to the epoxide on Ag(110). Furthermore, the presence of Cs on Ag(111) does not appear to affect either the amount of epoxide formed or activation energy of the lowest-energy pathway. Thus, electronic effects acting on the reaction itself do not appear to be significant.
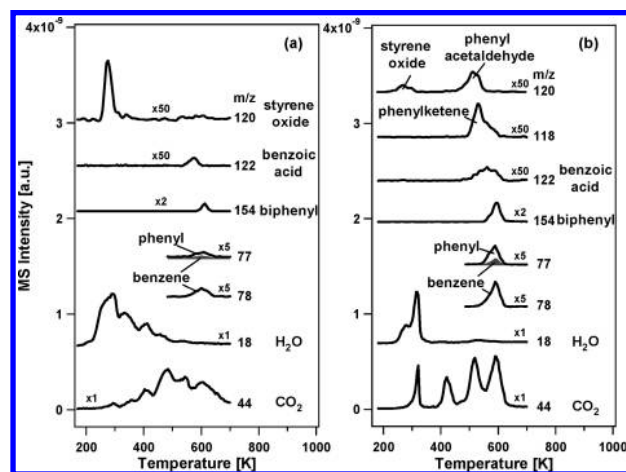

Figure 1. Temperature-programmed reaction spectra of styrene reacting with (a) an oxygen/cesium (0.1 ML)-cocovered Ag(110) surface and (b) an oxygen-precovered Ag(110) surface without Cs. Styrene was dosed at 170 K. The heating rate was 4 K/s.

A common reaction mechanism accounts for the strong structure sensitivity in the partial oxidation of styrene on both Ag(111) and Ag(110).[15] Styrene reacts with atomic oxygen to form an oxametallacycle intermediate. On Ag(111), the oxametallacycle preferentially undergoes ring closure to form styrene oxide, while on Ag(110), its transformation to a secondary intermediate via β-H elimination dominates, leading predominantly to the production of phenylacetaldehyde and phenylketene. The origin of the structure sensitivity is that on Ag(110), the activation energy for transformation of the oxametallacycle to the secondary intermediate is much lower than on Ag(111), so ring closure of the oxametallacycle to form styrene oxide is short-circuited.[15] The identity of these intermediates and their relative stabilities on the two surfaces have been established previously using X-ray photoelectron spectroscopy.[16]

The atomic structures of the clean Ag(110) surface (Figure 2a) and the 0.1 ML Cs-covered Ag(110) surface (Figure 2c) were imaged by STM at room temperature. The adsorption of cesium led to an increase in the corrugation of the (110) surface, forming a so-called missing-row-type (1 × 2) reconstruction. This direct imaging of the reconstruction is consistent with low-energy electron diffraction[17,18] and X-ray diffraction[19] studies. The STM study also revealed that both Cs and Ag atoms are mobile in the reconstructed top layer of Ag(110).[20] Cesium atoms move rapidly in the trough along the [1$\bar{1}$0] direction at room temperature. The fact that the entire surface is reconstructed at a cesium coverage of only 0.1 ML indicates that cesium atoms exert a cooperative effect on Ag(110). Figure 2b,d shows atomic models of the clean and Cs-covered surfaces, respectively. It is seen that the Cs-reconstructed Ag(110) surface effectively exposes microfacets of the (111)
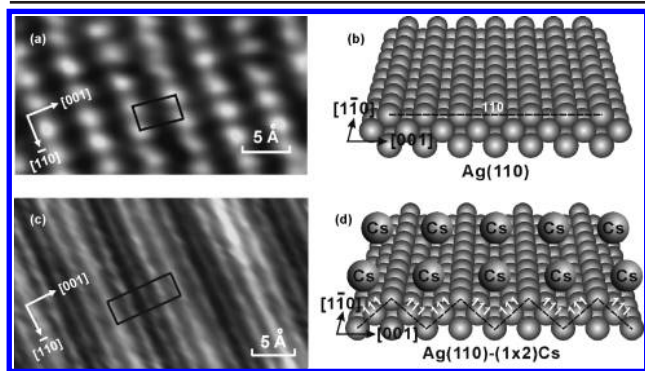
Figure 2. (a, c) Atomic-resolution STM images and (b, d) corresponding ball models of (a, b) the clean Ag(110) surface and (c, d) the 0.1 ML Cs-reconstructed Ag(110) surface.
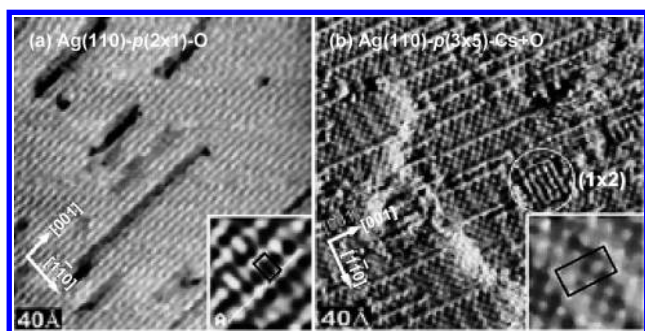

Figure 3. High-resolution STM images of (a) $p(2 \times 1)$-O on Ag(110) and (b) $p(3 \times 5)$-O on 0.1 ML Cs-reconstructed Ag(110).[20] The inset in each image shows the details of the unit cell. Copyright (2009) Elsevier.

surface. Clearly, the adsorption of small amount of cesium significantly changes the surface structure of Ag(110).

The cesium-induced reconstruction also alters the structure of the surface oxide on Ag(110).[20] Figure 3a shows the (2×1) added-row reconstruction on Ag(110) induced by chemisorbed oxygen. Adsorption of oxygen on the 0.1 ML Cs-reconstructed Ag(110) surface leads to a complex reorganization (Figure 3b) that exhibits domain walls along the [001] direction separating small domains with a (3×5) local ordering. Enlargement of the image (Figure 3b inset) shows that this (3×5) ordering is superimposed on the (111) microfacets. In this image, a patch of cesium-induced (1×2) reconstruction is still visible in the STM image (circled area). The atomic model of this surface is still under investigation. The domain walls along the [001] direction may comprise the localized cesium atoms bound to oxygen, as the density of these features corresponds to the Cs coverage. The (3×5)-ordered structures

are formed by surface oxide superimposed on (111) microfacets. The previous STM study suggests that mass transport of silver atoms is involved in the formation of the (3×5)-O structure on the Cs-reconstructed Ag(110) surface and that the (3×5)-O structure incorporates $^1/_3$ ML of silver adatoms.[20] Certainly, added silver atoms in the adsorbate layer would increase the complexity of the structure. A small amount of cesium significantly changes the structure of surface oxide on Ag(110), which may also alter the energy barriers of the surface reactions. Most significantly, the surface oxide on Cs-reconstructed Ag(110) is superimposed on the highly corrugated Ag(111) microfacets, which leads to a reactivity very similar to that of the extended (111) surface.

In conclusion, low surface concentrations of adsorbed cesium exert a cooperative effect on the surface structure of Ag(110), reconstructing the entire surface into (111) microfacets. This reconstruction switches the dominant products in the partial oxidation of styrene from phenylacetaldehyde and phenylketene to styrene oxide, the product observed on Ag(111) surfaces.

Supporting Information Available: Details for the experimental section and Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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