

Selectivity Limitations in the Heterogeneous Epoxidation of Olefins: Branching Reactions of the Oxametallacycle Intermediate in the Partial Oxidation of Styrene

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The partial oxidation of alkenes, particularly of ethene to ethene oxide, is an important process in industrial chemistry.¹ While several groups observed the Ag-catalyzed epoxidation of higher olefins in transient experiments,² little success is reported from steady-state reaction studies.³ Relatively little is known so far about the partial oxidation of larger alkenes and about the influence of functional groups on reaction products and selectivities. In this respect, previous workers have proposed that an oxametallacycle is the reactive intermediate in alkene epoxidation.^{4,5} In this communication, we present evidence that this intermediate may affect reaction channels that limit the selectivity of epoxidation, even for olefins without allylic hydrogens.

We present here a temperature-programmed reaction spectroscopy (TPRS) and X-ray photoelectron spectroscopy (XPS) study of the reaction of styrene with coadsorbed O on the Ag(111) surface. In contrast to previous publications on styrene epoxidation on Ag(111)^{2b} and Ag(110)^{2c} that reported styrene oxide as the only partially oxidized reaction product, we find the formation of benzene and benzoic acid in addition to styrene oxide and the combustion products water and CO₂. This difference will be discussed in detail elsewhere.

All experiments were done under ultrahigh vacuum conditions. We prepared the Ag(111)-p(4 × 4)-O by exposing the clean Ag(111) surface to NO₂ at 500 K.⁶ XPS spectra were acquired with a hemispherical electron energy analyzer using Mg K α X-rays as excitation source. All binding energies are referenced to the Ag 3d_{5/2} peak at 367.9 eV. The heating rate during TPRS measurements varied between 8 K/s at 150 K and 6 K/s at 600 K.

TPRS after exposure of the Ag(111)-p(4 × 4)-O surface to styrene at 160 K shows the evolution of CO₂ (*m/z* 44), water (*m/z* 18), styrene (*m/z* 104 and fragment 78), styrene oxide (*m/z* 120), benzene (*m/z* 78), and benzoic acid (*m/z* 122) (Figure 1). Styrene desorbs from the multilayer at 200 K and from the monolayer at 260 K. Both styrene desorption peaks are clearly visible in the data for the styrene parent mass *m/z* = 104 and the fragment *m/z* = 78. No peak is observed for *m/z* = 104 at 580 K. CO₂ desorbs in three major peaks at 320, 400, and 590 K. Water peaks are located at 320 and 370 K. Partially oxidized products form at 330 and 580 K. On the basis of its fragmentation pattern, we identified the reaction product formed at 330 K as styrene oxide. The formation of styrene oxide isomers, phenylacetaldehyde and acetophenone, can be excluded (see Supporting Information). Analysis of the fragmentation patterns shows that both benzene and benzoic acid are formed at 580 and 590 K, respectively. The ratio of benzoic acid to benzene formation is about 1:30. All preadsorbed O is consumed in the reaction.

To aid the identification of reaction intermediates, we exposed the Ag(111)-p(4 × 4)-O surface to styrene at 160 K, annealed it to increasing temperatures, and obtained XPS spectra. The main C 1s peak is observed at 284.2 eV after annealing to 280 K (bottom

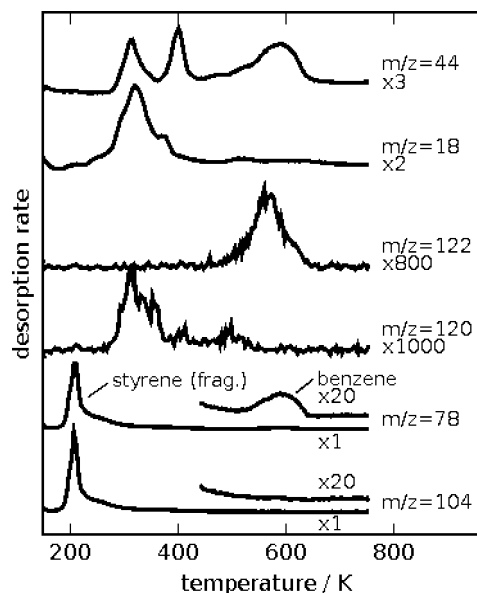


Figure 1. TPRS of the reaction of a styrene multilayer with the Ag(111)-p(4 × 4)-O. The graph shows the mass spectrometer signals for the parent masses of styrene (*m/z* 104), styrene oxide (*m/z* 120), benzoic acid (*m/z* 122), water (*m/z* 18), and CO₂ (*m/z* 44) as function of the temperature. The *m/z* 78 signal is the parent mass of benzene as well as a fragment of styrene and benzoic acid. The data have not been corrected for the different sensitivities of the mass spectrometer for the reaction products.

curve in Figure 2). A shoulder can be seen on the higher binding energy side of the main peak at 285.7 eV. After annealing to 380 K, the main C 1s peak shifts to 284.1 eV. More importantly, the shoulder at 285.8 eV loses most of its intensity, and an additional peak appears at 287.3 eV. Further annealing to 480 K to isolate the intermediates responsible for the products evolving near 600 K causes only small changes in the XPS spectrum (not shown).

Recent studies suggest the formation of an oxametallacycle during the Ag-catalyzed epoxidation of ethene⁴ and styrene.⁵ Barteau et al. prepared a styrene-based oxametallacycle by adsorbing styrene oxide on clean Ag(111).⁵ Their synchrotron-based XPS data give a binding energy of 283.8 eV, attributed to C atoms in the phenyl group, and a feature at 1.0 eV higher binding energy, attributed to the C atom bound to the O in the oxametallacycle.^{5a} Similar results are reported for ethene oxide adsorption on Ag(111).⁷ The high binding energy shoulder in our data after annealing to 280 K (Figure 2) corresponds to a peak located about 1.5 eV above the C 1s main peak. The overlap of this feature with the main C 1s peak makes a precise determination of the chemical shift impossible. Nevertheless, we suggest that the high binding energy component observed at 285.7 eV after annealing to 280 K originates from an oxametallacycle.

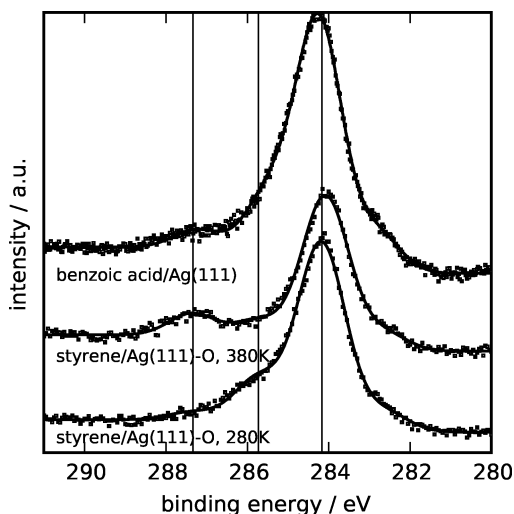
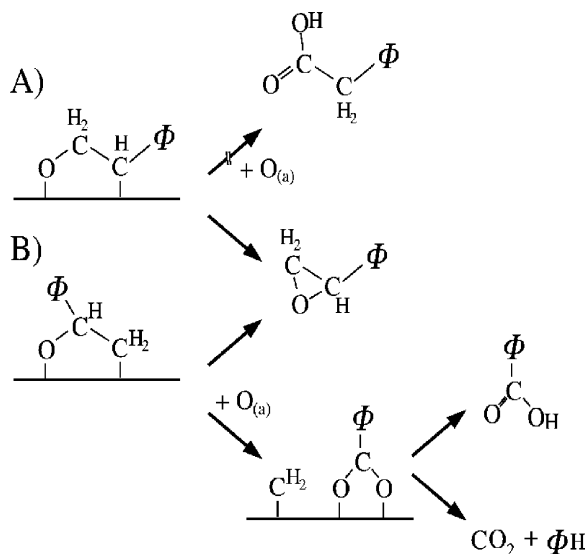


Figure 2. XPS of styrene dosed on the Ag(111)-p(4 × 4)-O surface at 160 K and annealed to 280 (lower curve) and 380 K (middle curve). The upper curve shows XPS obtained from a Ag(111) sample exposed to benzoic acid at 400 K.

Scheme 1. Reaction Intermediates and Products



The binding energy difference of 3.2 eV between the main C 1s peak and the higher binding energy peak at 287.3 eV found after annealing to 380 K is close to the value of 3.0 eV obtained after exposing the clean Ag(111) surface to benzoic acid at 400 K to form benzoate (upper curve in Figure 2) and is similar to the chemical shift of 2.8 eV reported for benzoate on Ni(110).⁸ It is also close to the value of 2.9 eV reported for acetate on Ag(110)⁹ and 3.2 eV for acetate on Ni(110).¹⁰ Therefore, we suggest that the intermediate formed after annealing to 380 K is benzoate.

Due to space limitations, we will discuss only the formation of the partially oxidized products. The lower temperature combustion products will be discussed elsewhere. In agreement with previous models for the epoxidation of olefins,^{4,5} Scheme 1 starts from the formation of an oxametallacycle through the asymmetric addition of O(a) to the C=C bond. The O atom can be attached either to

the terminal C atom of the alkyl group (linear configuration, Scheme 1.A) or to the second C atom (branched configuration, Scheme 1.B). Both configurations may form styrene oxide.

Our results indicate that benzene and benzoic acid, which severely limit the selectivity of the partial oxidation of styrene, are formed as the result of attack of electron-deficient C in the oxametallacycle by adsorbed O (Scheme 1). The C atom attached to the oxametallacycle O in the branched configuration is particularly susceptible to a nucleophilic attack by O(a) because both the O atom and the phenyl group are electrophilic. This reaction forms benzoate, which ultimately reacts to either benzoic acid or benzene and CO₂. Indeed, we observed a CO₂ to benzene ratio of 1:1 at 580 K (see Supporting Information). The reaction at the electrophilic C of the metallacycle is quite similar to the attack of adsorbed O on 1,2-ethanedioxy¹¹ and on the ring-opened, partially oxidized intermediate in furan oxidation on Ag(110)¹² which limits the oxidation selectivity of ethylene glycol to glyoxal and furan to maleic anhydride, respectively.^{12,13} A nucleophilic attack of the linear configuration by O(a) would likely yield phenylacetic acid, which was not detected in our experiments on Ag(111). It should be noted that phenylacetic acid as well as styrene oxide and benzoic acid are formed during the reaction of styrene with coadsorbed O on Au(111).¹⁴ The relatively high decomposition temperature of the benzoate compared to the temperature at which styrene oxide is formed likely results in the blocking of active sites during steady-state reactions at lower temperatures or higher pressures. This may explain the previously reported relatively slow steady-state oxidation of styrene over Ag.³

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation (NSF CHE 9820703). We also acknowledge fruitful discussions with X. Deng, C. M. Friend, and A. R. Alemozafar.

Supporting Information Available: Analysis of the fragmentation pattern observed during TPRS. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA054845S