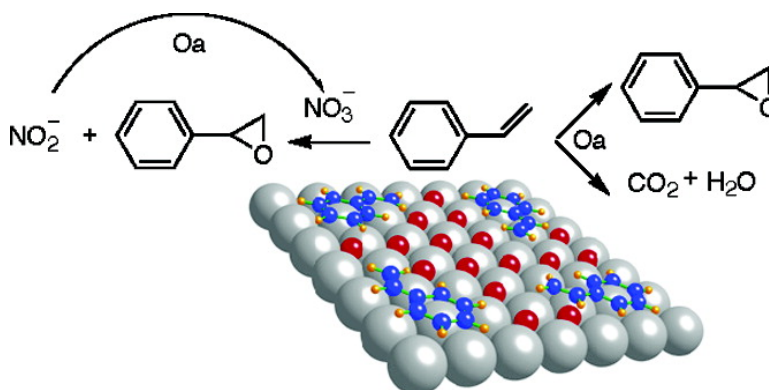Article

Mechanism, Selectivity Promotion, and New Ultraselective Pathways in Ag-Catalyzed Heterogeneous Epoxidation

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Mechanism, Selectivity Promotion, and New Ultraselective Pathways in Ag-Catalyzed Heterogeneous Epoxidation

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Abstract: The selective oxidation of styrene on clean and modified Ag(100) surfaces has been studied by synchrotron fast XPS and temperature-programmed reaction spectroscopy. By following the time dependence of surface species, it is unequivocally demonstrated that the necessary and sufficient conditions for epoxide formation are oxygen adatoms and π-adsorbed alkene molecules. Increased oxygen coverage and coadsorbed Cs have pronounced and opposite effects on epoxidation selectivity, consistent with the view that the valence charge density on O_a is pivotal in determining this property. Submonolayer quantities of Cs nitrate generated in situ open a new, low-temperature ultraselective, epoxidation pathway thought to involve direct oxygen transfer from the oxyanion to the alkene.

Introduction

The silver-catalyzed heterogeneous epoxidation of ethene continues to attract fundamental and applied research[1] because the process is both mechanistically interesting and technologically important. Extension of this chemistry to the efficient epoxidation of higher terminal alkenes, for example, propene, is a challenging unsolved problem whose solution requires a secure understanding of elementary reaction steps. Single-crystal studies have played an important role in clarifying the molecular mechanism of alkene epoxidation[2] and in elucidating the role of electronegative[3] and electropositive promoters.[4] The identity of the adsorbed oxygen species responsible for ethene epoxidation and combustion was the subject of a long-standing controversy. According to one influential view,[5] adsorbed dioxygen is the epoxidizing agent, whereas oxygen adatoms (O_a) are responsible for combustion. An alternative hypothesis,[6] also based on classical measurements, is that all of the chemistry is due to O_a, thought to undergo either Eley−Rideal or Langmuir−Hinshelwood reactions with ethene, resulting in epoxidation or combustion, respectively. Single-crystal measurements based on similar methodologies led to strongly divergent conclusions: Campbell and Koel[7] inferred that dioxygen was indeed the selective oxidant; on the other hand, Grant and Lambert[4] claimed that O_a reacted with adsorbed ethene to yield both the epoxide and the combustion products.

Ethene itself adsorbs weakly on Ag surfaces, which precludes temperature-programmed reaction (TPR) studies under ultrahigh vacuum conditions—the molecule desorbs before it can react. Therefore, higher terminal alkenes that bind sufficiently strongly have been used instead, including norbornene,[8] 1-butene,[9] 2-methylpropene,[10] 3,3-dimethyl-1-butene,[11] butadiene,[12,13] and, especially, styrene (phenyl-ethene).[14−16]

Of these model alkenes, styrene may be regarded as the most important because its chemisorption geometry on silver, determined by NEXAFS, is that of a planar molecule lying parallel to the metal surface with preservation of the olefinic double bond.[17] In particular, we found no tilting or out-of-plane twisting of the olefin function that could endow styrene with reactive properties significantly different from those of ethene which adsorbs with its C=C bond parallel to the metal surface.[18] This validates the use of styrene as a model terminal alkene for epoxidation studies on silver surfaces.

Here, using synchrotron XPS to follow the time dependence of surface species, we provide the first direct demonstration that the minimum necessary and sufficient conditions for the epoxidation of styrene are the π-adsorbed alkene and oxygen adatoms (O_a)—no other forms of oxygen were detectable under our conditions, neither dioxygen, nor subsurface or oxide-like

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oxygen. These results constitute conclusive evidence that the epoxidizing species is O_a, hopefully laying this issue to rest once and for all. We also show that the opposite effects on selectivity of Cs and of increasing oxygen coverage are in excellent accord with the atomic oxygen hypothesis, proposed long ago, according to which electronic effects are of pivotal importance. Finally, we demonstrate that the presence of submonolayer quantities of Cs nitrate opens a new ultraselective epoxidation channel.

Experimental Methods

TPR Experiments. These measurements were carried out in Cambridge in a UHV chamber of conventional design operated at a base pressure of 1×10^{-10} mbar; this apparatus, including the methods of sample mounting, manipulation, and cleaning, has been described in detail elsewhere.[19] Reagent grade styrene was outgassed by means of five freeze−pump−thaw cycles and was delivered to the sample via a tube doser; oxygen exposures were carried out by backfilling the vacuum chamber. Styrene oxide dosing was not possible in this apparatus due to extensive decomposition of the vapor in the gas lines. TPR spectra were acquired at a heating rate of 5 K s^{-1}, while monitoring the relevant masses by means of a quadrupole mass spectrometer whose ionizer was located ∼2 cm from the crystal face. Control experiments showed that with this geometry essentially all of the detected species arose from the front face of the sample. Selectivity toward styrene epoxide formation was calculated from the TPR integrated desorption yields of styrene epoxide (91 m/z) and H_2O (18 m/z), after correction for instrumental sensitivity.

TP-XPS Experiments. Temperature-programmed X-ray photoelectron spectroscopy (TP-XPS) measurements were carried out at the SuperESCA beamline at the ELETTRA synchrotron radiation facility, Trieste, Italy. The XP spectra were collected using a double pass hemispherical electron analyzer with a 32-channel detector. Surface order and cleanliness were checked by LEED and XPS, respectively. Surface reaction experiments were performed by adsorbing oxygen and styrene, then ramping the temperature while acquiring the C 1s or O 1s XP spectra. The rate of data acquisition was typically ∼60 s/spectrum. Given that the heating rate for TP-XPS experiments (∼0.3 K/s) was lower than that in the TPR experiments (∼5 K/s), the desorption temperatures in the former case would be 20−30 K lower than in the latter case. Quoted styrene coverages were determined by XPS with reference to the known[20] saturation coverage of atomic oxygen on Ag(100): 0.5 monolayers (ML) (1 ML is defined as the number of silver atoms in the first layer of the Ag(100) surface), as described in detail by Solomon et al.[21] Calibration was achieved by comparing the 0.5 ML O 1s intensity with that from a styrene-saturated overlayer, due allowance being made for photoionization cross sections[22] and variations in photon flux.

Results and Discussion

Temperature-Programmed Reaction. In the absence of coadsorbed oxygen, styrene adsorbs and desorbs reversibly from Ag(100) without deposition of carbon or desorption of any other species.[17] Coadsorption with oxygen leads to oxidation products as illustrated by the following TPR results. Figure 1A,B shows a set of TPR spectra obtained after adsorption at 200 K of 0.035 ML (A) and 0.16 ML (B) of oxygen, then ∼0.04 ML of styrene, followed by a temperature ramp. Under these conditions, the only gaseous products were CO_2, H_2O, and styrene epoxide,

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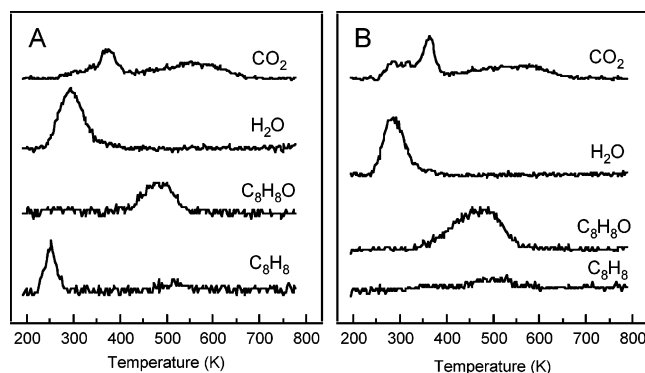(22) Yeh, J. J.; Lindau, I. *At. Data Nucl. Data Tables* **1985**, *32*, 1−155.

Figure 1. TPR spectra showing reaction products from coadsorbed styrene (∼0.04 ML) and atomic oxygen on Ag(100) in the presence of (A) 0.035 ML, and (B) 0.16 ML of atomic oxygen.

detected at $m/z = 44$, 18, and 91, respectively. Unambiguous identification of styrene epoxide was provided by the fragment ion spectra at $m/z = 39$, 65 which mirrored the $m/z = 91$ spectra.[14] Figure 1 demonstrates that reaction of styrene with preadsorbed atomic oxygen led to both selective oxidation (styrene oxide) and total combustion.

Three points should be noted. (i) With an initial oxygen coverage of 0.035 ML, desorption of unreacted styrene occurred. However, with higher oxygen coverage (0.16 and 0.3 ML (Figure 4)), styrene conversion was complete. (ii) Styrene desorption gives a peak at 250 K (oxygen coverage 0.035 ML), whereas reactively formed styrene oxide gives a peak in the range 420−480 K depending on the initial oxygen coverage. Thus, O_a must react irreversibly with coadsorbed styrene at temperatures below 250 K along the pathway to styrene oxide. The identity of the adsorbed species that leads to evolution of gaseous styrene oxide, be it molecular styrene oxide or an oxametallacycle, cannot be determined from either the TPR or the XPS results. Accordingly, we refer to this species as "adsorbed styrene oxide". (iii) The water TPR spectrum exhibits a peak at 280 K. Production of water is thought to be initiated by H-abstraction from the alkene and/or the adsorbed epoxide (i.e., we cannot exclude the possibility of some epoxide combustion) by O adatoms[2,9,10] followed by $OH_a + OH_a \rightarrow H_2O + O_a$. The remaining carbonaceous fragments then react further with O_a to form CO_2: the corresponding desorption trace exhibits greater complexity than the other three, with distinct maxima at 300, 360, and 550 K, presumably reflecting successive stages in the combustion of the carbonaceous residues. Gaseous H_2O and CO_2 are both formed by surface reaction rate-limited processes—the desorption temperatures of adsorbed water and adsorbed CO_2 from silver are ∼160 and <160 K, respectively.[23] Because water production is complete by 350 K, the later stages of CO_2 formation cannot be due to combustion of adsorbed styrene oxide at temperatures >350 K as there is no water observed here (recall there is no styrene present at this temperature). Accordingly, the "late" CO_2 is assigned to reaction of O_a with the carbonaceous residues resulting from H-stripping of the alkene and/or the adsorbed epoxide.

Temperature-Programmed X-ray Photoelectron Spectroscopy. The top panel of Figure 2 shows C 1s and O 1s XP spectra obtained after 200 K dosing of clean Ag(100) with 0.3

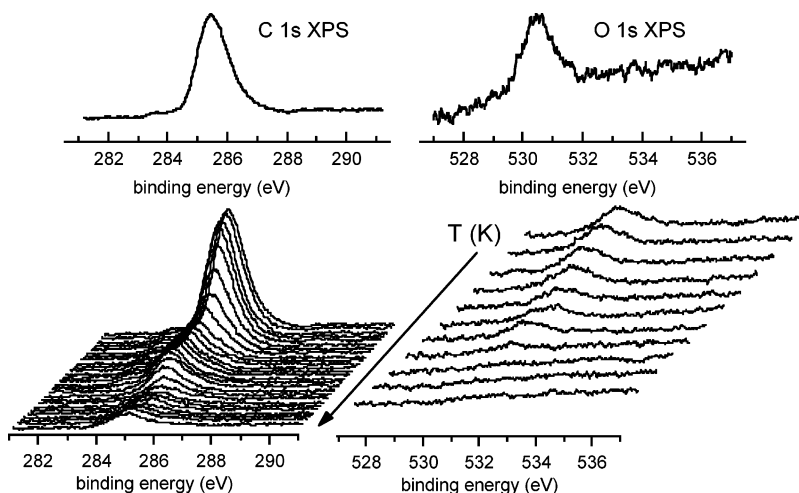(23) Bowker, M.; Barteau, M. A.; Madix, R. J. *Surf. Sci.* **1980**, *92*, 528−548.

Figure 2. Top: C 1s and O 1s XPS spectra after adsorbing 0.3 ML of oxygen and then ~0.1 ML of styrene on Ag(100) at 200 K. Bottom: C 1s and O 1s XP spectra as a function of increasing temperature.
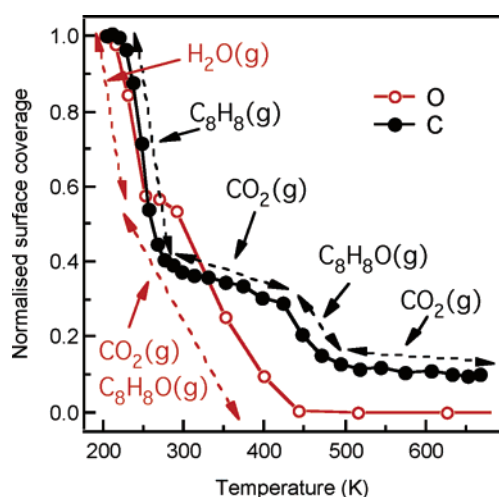

Figure 3. C 1s and O 1s normalized integrated intensities resulting from reaction of ~0.1 ML of styrene with 0.3 ML of oxygen in the interval 205−667 K.

ML of oxygen followed by ~0.1 ML of styrene. These spectra indicate the presence of (i) a single oxygen species with a binding energy (BE) of 530.3 eV which corresponds to chemisorbed atomic oxygen[24] and (ii) a single carbon species with a BE of 285.4 eV corresponding to chemisorbed styrene;[17] the vinyl and phenyl carbons could not be resolved.[17] At this stage, no other species were present on the sample surface. (In repeated experiments, a very small feature at 283.5 eV appeared intermittently, disappearing at ~320 K; it may have been due to styrene adsorbed at defect sites.)

The bottom panel of Figure 2 shows the subsequent time evolution of the C 1s and O 1s XP spectra when the temperature was ramped from 205 to 667 K (C 1s data at ~0.3 K s^{-1}, ~67 s/spectrum and O 1s data at ~0.1 K s^{-1}, ~300 s/spectrum). The interpretation of these results should be consistent with the TPR data. In principle, one might expect to distinguish at least three different carbon-containing surface species: styrene, styrene epoxide, and carbonaceous fragments, as the surface reaction between styrene and coadsorbed atomic oxygen takes place. CO_2 should not be detected because it desorbs im-

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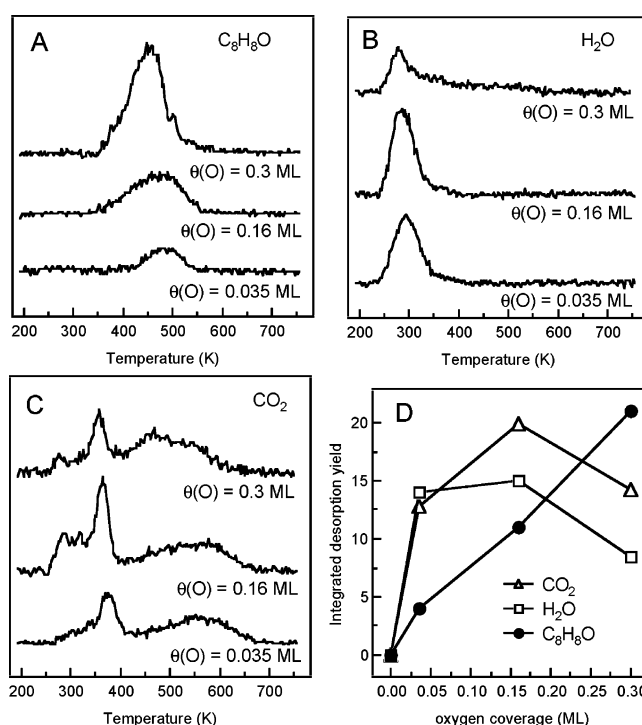
Figure 4. Effect of increasing oxygen coverage on product distribution (0.035, 0.16, and 0.3 ML of oxygen followed by ~0.04 ML of styrene).

mediately upon formation, as the TPR results demonstrate. At 205 K, the C 1s spectrum consisted of a single peak with BE = 285.4 eV corresponding to adsorbed styrene. As the temperature was increased to 340 K, the BE shifted to 285 eV: at this point, the only carbon-containing species should be adsorbed styrene epoxide which desorbs at ~450 K and carbonaceous fragments (styrene itself desorbs at ~250 K). Although at this temperature more than one carbon-containing surface species was present, we could not resolve them with confidence: hence, the total integrated C 1s intensity is presented instead. At 650 K, where only the carbonaceous fragments remained, the C 1s BE was 285 eV. H_2O was not detectable, because, like CO_2, it desorbed immediately upon formation. The C 1s BEs for absorbed styrene and styrene oxide were 285.4 and ~285 eV, respectively: on the basis of initial state effects, this is the opposite of expectation and could indicate that the adsorbed

precursor to gaseous styrene oxide is something other than an intact styrene oxide molecule. If, however, final state effects are of importance, because there is no simple correspondence between the magnitude of such effects and the molecular structure of chemisorbed species, no conclusions may be drawn from this observation.

Figure 3 shows the normalized integrated O 1s and C 1s XP intensities as a function of temperature, taken from the raw O 1s and C 1s data shown in Figure 2. Consider first the behavior of the O 1s intensity, which is given by the red curve in Figure 3. This quantity is proportional to the coverage of all oxygen-containing surface species, so the observed profile reflects stages in the desorption of H_2O, CO_2, and C_8H_8O. The O 1s intensity remained constant from 200 to 215 K. The subsequent sharp decrease corresponds to desorption of H_2O commencing at ~230 K, consistent with the TPR results. Comparison with Figure 1, allowing for the difference in heating rates between the TPR and TP-XPS measurements, indicates that over the interval ~230 to ~250 K water desorption would have been completed. CO_2 started to desorb at ~260 K, while styrene epoxide was retained on the surface. The intensity decrease between ~300 and ~425 K is due to CO_2 desorption, followed by styrene oxide desorption (~425 to ~475 K) and the final stages of CO_2 desorption.

The C 1s integrated intensity profile is shown in Figure 3 by the black curve. Given the initial conditions (0.1 ML of styrene; 0.3 ML of oxygen), desorption of unreacted styrene is expected, so that the observed intensity decreases correspond to loss of C_8H_8, CO_2, and C_8H_8O. After remaining constant from 205 to 220 K, the intensity decreased sharply between 220 and ~260 K, consistent with desorption of styrene (TPR peak at 250 K); beyond this point, the only carbon-containing species left on the surface should be styrene oxide and carbonaceous fragments. From ~260 to ~400 K, the C 1s signal continued to decrease, but at a lower rate. This decrease corresponds to combustion of carbonaceous fragments and the consequent desorption of CO_2 (first and second TPR peaks at ~300 and ~360 K). From ~400 to ~500 K, there is a second sharp decrease in the C 1s signal which corresponds to desorption of styrene oxide (TPR peak at ~450 K). At ~500 K, the only remaining surface species are carbonaceous fragments. From ~500 to ~650 K, the C 1s signal decreases only slightly as there is very little combustion of the carbonaceous species to CO_2 (third TPR peak at ~550 K). Notice the good agreement between the TPR and C 1s XPS results—Figure 3 shows that the maximum desorption rates of the reactant and product occur at ~240 and ~450 K, respectively; this compares favorably with Figure 1, which shows styrene and styrene epoxide peaks at corresponding temperatures. Furthermore, Figure 3 also shows that ~10% of the original carbon remained on the surface as carbonaceous species.

The TPR and TP-XPS results shed light on the mechanism of this surface reaction. Styrene reacts with O_a to form adsorbed styrene oxide at temperatures <250 K. H_2O desorption (TPR peak at 280 K) ceases at the point where CO_2 desorption has only just begun (Figure 1). This implies a mechanism whereby styrene and/or styrene oxide molecules are quickly stripped of all their H atoms, yielding water, followed by oxidation of the residual carbon skeleton to CO_2, predominantly at higher temperatures. Although the results do not permit a determination of the relative importance of styrene versus styrene oxide

Scheme 1
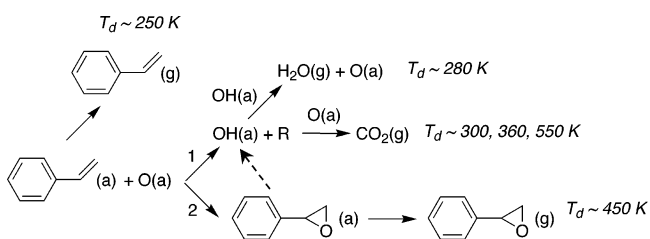
combustion, note that substantial CO_2 production occurs after completion of H-stripping, when the only C-containing surface species are carbonaceous fragments and styrene oxide (Figure 1). Because production of >350 K CO_2 is not accompanied by production of H_2O, it follows that this CO_2 cannot be due to combustion of adsorbed styrene oxide—that is, the epoxide does not burn at relatively high temperatures. Therefore, intuition suggests, although we cannot prove, that the epoxide is unlikely to burn at <350 K. If correct, this implies that all combustion is associated with styrene burning and that the epoxide is immune to combustion under these conditions. In Scheme 1, this is signified by the dashed arrow associated with the epoxide combustion pathway.

The TPR and XPS data are in principle consistent with the possibility that styrene oxide and all of the combustion products are formed from a common surface intermediate: adsorbed styrene oxide. We do not favor this interpretation because it does not provide an explanation for the dramatic and opposite effects of chlorine and alkali on the selectivity of styrene epoxidation on single-crystal silver.[14] On the other hand, the view that electropositive and electronegative species should have opposite effects on the branching ratio of the two alternative first steps (1,2) shown above provides a straightforward rationalization. It also does not preclude the possibility that some CO_2 and water are formed from adsorbed styrene epoxide.

It has recently been proposed[25,26] that alkene epoxidation proceeds via an oxametallacycle intermediate that may decompose to yield either epoxide or combustion products. We cannot rule out the possibility that styrene oxide is adsorbed as an oxametallacycle. Whatever its chemical state, the argument outlined above implies that adsorbed styrene epoxide is not a major source of combustion products. The observed effect of electronegative and electropositive species on epoxidation selectivity may be rationalized straightforwardly in terms of parallel epoxidation and combustion pathways for the alkene, as discussed below. On the other hand, there appears to be no simple way of accounting for these effects in terms of the "metallocycle common intermediate" mechanism. More refined experiments supported by detailed calculations should resolve the issue.

Effect of Electronegative and Electropositive Species on Epoxidation Selectivity. The effect of increased coverage of preadsorbed O_a on product distribution is illustrated in Figure 4. Panels A,B,C show the behavior of C_8H_8O, H_2O, and CO_2, respectively; panel D shows the corresponding integrated desorption yields. It is clear that the selectivity toward epoxide formation increases with oxygen coverage; in particular, on going from 0.16 to 0.3 ML of oxygen, the yield of epoxide doubles, whereas those of the combustion products actually fall.

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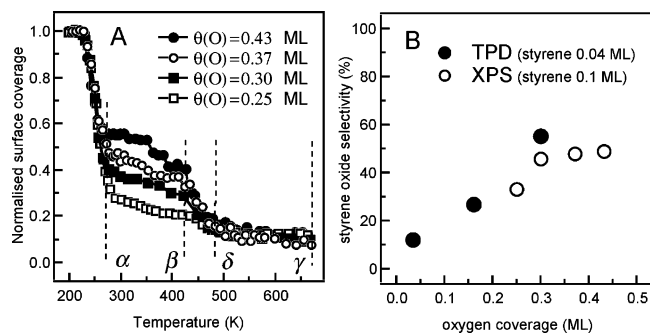(26) Linic, S.; Barteau, M. A. *J. Catal.* **2003**, *214*, 200−212.

Figure 5. (A) Normalized C 1s XP integrated intensity as a function of temperature after dosing ∼0.1 ML of styrene on an oxygen predosed Ag-(100) surface. (B) Selectivity toward styrene epoxide formation estimated from Figure 4D (TPR data) and Figure 5A (TP-XPS data).

Figure 6. TPR spectra obtained after adsorbing 1 L of styrene and 100 L of O_2 on Ag(100) precovered with: (A) 0.035 ML of Cs, and (B) 0.07 ML of Cs.

Figure 5A shows results derived from a series of temperature-programmed XPS measurements using four different initial oxygen coverages and an approximately constant styrene coverage of ∼0.1 ML (obtained by using a fixed styrene dose). It is clear that as the oxygen coverage increased the conversion of styrene also increased, because (i) the amount of unreacted styrene decreased, and (ii) the amounts of adsorbed styrene oxide and carbonaceous species increased. The selectivity toward styrene epoxide formation may be estimated from these results as follows. The Greek letters in Figure 5A designate the temperatures corresponding to the various breaks in the C1s integrated intensity curve; $\theta(i)$ represents the coverage of carbon-containing species at temperature i. By point α in Figure 5A, all of the unreacted styrene had desorbed. The intensity at this point is a measure of the amount of styrene oxide and carbonaceous species present, before any CO_2 desorption had occurred, and is $\theta(\alpha)$. If we assume that the difference $[\theta(\beta) - \theta(\delta)]$ between the second break (β in Figure 5A) and the third break (δ in Figure 5A) corresponds to the total amount of styrene oxide that desorbed from the surface at ∼450 K, then the selectivity toward epoxide formation is given by $[\theta(\beta) - \theta(\delta)]/\theta(\alpha)$. (The assumption is reasonable, given that (i) styrene epoxide desorbs at ∼450 K and (ii) the decrease in C 1s signal will be much greater for desorption of styrene and styrene oxide than for CO_2—8 versus 1 carbon atoms leaving the surface.) Figure 5B shows the selectivity calculated on this basis using the four sets of XPS data (○). Also shown are selectivities calculated from the TPR data illustrated in Figure 4 (●). This figure demonstrates unequivocally that increasing the oxygen coverage resulted in a substantial increase in selectivity toward styrene epoxide formation. To our knowledge, these results provide the first demonstration of the effect of oxygen coverage on styrene epoxidation selectivity. Because 20 oxygen atoms are required for the complete combustion of one styrene molecule, whereas only one O_a is needed to epoxidize styrene, one might naively suppose that increased oxygen coverage would favor combustion at the expense of epoxidation. In fact, the opposite effect is observed, and it may be rationalized as follows. Atomic oxygen is an electronegative adsorbate on silver surfaces. With increasing O_a coverage, the extent of charge transfer from Ag to each individual oxygen atom decreases, thereby favoring electrophilic attack by these species on the adsorbed alkene, which leads to epoxide formation.[2] Thus, we may say that oxygen itself acts as an electronic promoter in much the same away as adsorbed chlorine. According to
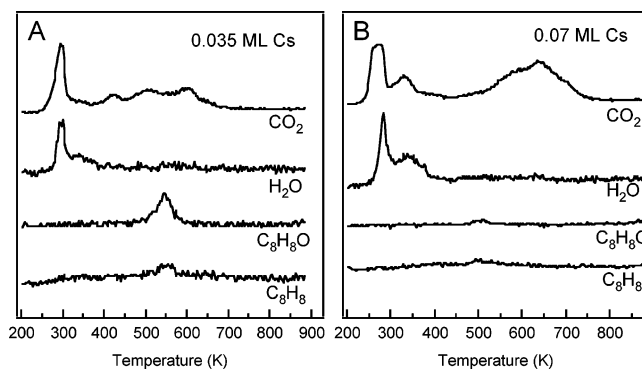
us,[2,4,11,13–15] it is the valence charge density on O_a that determines its electrophilicity and hence the relative rates of the epoxidation and combustion reactions. This view is consistent with the recently reported[3] relative promoting efficiencies of adsorbed F, Cl, Br, and I on epoxidation selectivity: the extent of promotion correlates with halogen electron affinity, showing a strong maximum at chlorine. Furthermore, it is also consistent with the effect of coadsorbed Cs on selectivity, described in the next section.

The results shown in Figure 5a can also be used as a check on the mass balance for the reaction. The above interpretation of the TP-XPS data implies that $[\theta(\alpha) - \theta(\beta)]$ and $[\theta(\delta) - \theta(\gamma)]$ correspond to desorption of CO_2, whereas $[\theta(\beta) - \theta(\delta)]$ corresponds to desorption of styrene oxide. Hence, the coverage of oxygen atoms consumed by the reaction (θ_O, the initial oxygen coverage) can be related to the initial styrene coverage (θ_C) by the relationship $\theta_O = \theta_C[20\theta(\alpha) - 19\theta(\beta) + 19\theta(\delta) - 16\theta(\gamma)]$ (assuming that there is no H left on the surface). The data fit this equation within 10%, further validating our interpretation.

Figure 6A (B) shows TPR spectra obtained after adsorbing 1 L (1 L = 10^{-6} Torr s) of styrene and 100 L of O_2 on Ag(100) precovered with 0.035 (0.07) ML of Cs. By comparison with Figures 1 and 4, it is clear that the presence of 0.035 ML of Cs caused a substantial decrease in epoxidation and an increase in combustion. Increasing the Cs coverage to 0.07 ML very strongly quenched epoxidation activity, resulting in almost 100% combustion. According to the argument advanced above, electropositive Cs adatoms should enhance charge transfer to O_a rendering it more nucleophilic, thus favoring H-abstraction from the alkene followed by deep oxidation. This view is very strongly supported by earlier work[14] on Ag(111) in which the dramatic and opposite effects of chlorine and alkali on the selectivity of styrene epoxidation were demonstrated: unpromoted Ag gave 60% selectivity; 0.33 ML of chlorine increased the selectivity to 93%; and 0.33 ML of potassium reduced the selectivity to 0%. (In passing, we note the well-known industrial practice of adding ppm levels of alkali to Ag/α-alumina catalysts to enhance selectivity, the distribution of alkali between the oxide and metal phases being unknown. This is a second-order effect principally involving neutralization of acid sites on the oxide support. Such sites would otherwise lead to isomerization of the epoxide to the aldehyde, followed by combustion.)
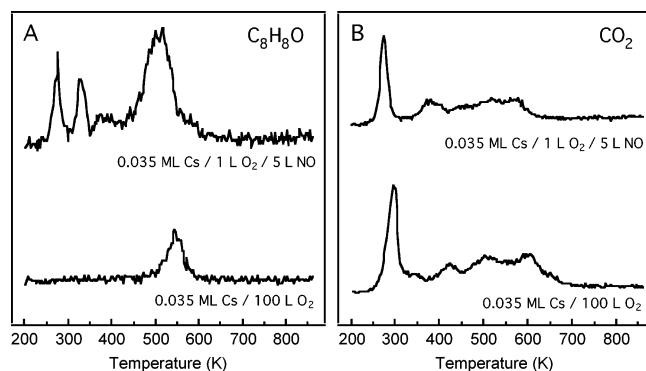
Figure 7. Styrene epoxide (A) and CO_2 (B) TPR spectra obtained after adsorbing 1 L of styrene (220 K) on Ag(100) after two different initial conditions: (i) 0.035 ML of Cs followed by 100 L of O_2, and (ii) 0.035 ML of Cs (300 K) followed by 1 L of O_2 (220 K) and 5 L of NO (220 K).

Effect of Simultaneous Presence of Cs and NO_x on Epoxidation Chemistry. Earlier work[27] on ethene epoxidation with a Ag(111) model catalyst operated at 10 mbar total pressure in a batch reactor demonstrated that the deliberate introduction of ppm levels of NO_x into the reaction gas resulted in significantly enhanced epoxidation selectivity, but only in the presence of submonolayer quantities of Cs, deposited by vacuum evaporation. Subsequently, by means of control experiments involving vacuum deposition of KNO_2 and KNO_3 on Ag(111), it was shown[28] that the dosing sequence K + O_2 + NO could be used to produce submonolayer amounts of alkali nitrate on the silver surface, accompanied by O_a.

In view of these findings, we investigated the properties of such nitrated surfaces toward styrene oxidation in a well-controlled UHV environment, something that had not been previously studied. The upper data set in Figure 7A,B was taken by dosing the cesiated (0.035 ML), oxygenated (100 L) Ag surface with NO (5 L) prior to styrene adsorption (1 L)—this procedure should lead to the formation of submonolayer amounts of $CsNO_3$ in the initial adlayer. The lower data set corresponds to a control experiment, identical in every respect, except that the NO dose was not applied.

The control experiment gave some styrene epoxide that desorbed at a temperature characteristic of reaction between styrene and O_a (~540 K) along with a lot of CO_2 (recall that the effect of Cs is to reduce epoxidation selectivity). Most interestingly, the result of NO pretreatment was to open up a new low-temperature selective oxidation channel—the epoxide peaks at 275 and 325 K along with a less pronounced feature at 380 K. (As expected, the pathway due to O_a still operated, producing the epoxide peak at ~500 K.) Moreover, the CO_2 fingerprint obtained in this case is very similar to that obtained in the control experiment. Therefore, it seems reasonable to

Scheme 2
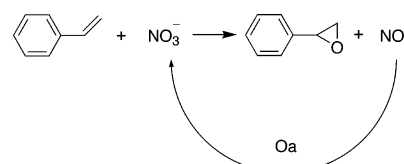
suppose that this CO_2 is very largely, if not entirely, due to surface species other than nitrate. If this supposition is correct, the implication is that the nitrate-induced epoxidation channel is close to 100% selective. Essentially the same behavior was observed over a range of Cs coverages, although the relative product yields were different

We suggest that the remarkable low-temperature epoxidation process involves direct transfer of oxygen to the alkene from adsorbed alkali nitrate with simultaneous conversion of the latter to nitrite. The results of recent DFT calculations are consistent with this proposal.[29] Under conditions of steady-state reaction, with reoxidation of nitrite to nitrate, the following catalytic cycle could therefore operate (see Scheme 2).

Finally, we attempted to confirm the "direct transfer from nitrate" hypothesis by means of ^{18}O isotope tracing experiments. Notionally, the relevant surface process corresponds to CsO_2^{30} + NO → $CsNO_3$. Therefore, we used $^{18}O_2$ and $N^{16}O$ in an attempt to generate $CsN^{16}O^{18}O_2$ with the hope of seeing 2:1 relative yields of $C_8H_8^{18}O$ and $C_8H_8^{16}O$ in the low-temperature epoxidation channel. The results were inconclusive because Cs-induced dissociation of NO[31] inevitably contaminated the surface with $^{16}O_a$. A more refined technique needs to be developed.

Conclusions

(1) The minimum necessary and sufficient conditions for the epoxidation of styrene on Ag(100) are π-adsorbed alkene and oxygen adatoms.

(2) Oxygen adatoms also lead to formation of H_2O and CO_2, the propensity toward epoxidation versus combustion being determined by the valence charge on O_a. This view is confirmed by the opposite effects on selectivity of increased oxygen coverage and coadsorbed Cs.

(3) The presence of submonolayer quantities of Cs nitrate opens a new, low-temperature, ultraselective epoxidation channel assigned to oxygen transfer from alkali nitrate to alkene.

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