Surface Chemistry

Ethylene Epoxidation on Ag: Identification of the Crucial Surface Intermediate by Experimental and Theoretical Investigation of its Electronic Structure**

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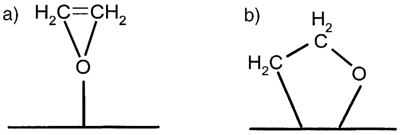
An important issue regarding the mechanism of heterogeneous epoxidation of ethylene on silver (Ag) is related to the formation of C–O bonds.[1–3] There are two possible ways for the C–O bonds to form: It is conceivable that the dominant pathway would proceed through either a concerted addition of surface oxygen to the C=C bond of ethylene or by sequential formation of the two C–O bonds by a creation of an asymmetric surface intermediate (Scheme 1).



Scheme 1. Possible intermediates in ethylene epoxidation on Ag: a) in the concerted addition of ethylene to oxygen and b) in the sequential formation of C–O bonds (surface oxametallacycle).

It has been shown previously in temperature-programmed desorption (TPD) experiments that a surface intermediate formed on Ag(111) upon adsorption of ethylene oxide (EO) at about 250 K under ultrahigh vacuum (UHV) conditions reacts at about 310 K to reform EO plus small amounts of other products, including ethylene.[4] High-resolution electron energy loss spectroscopy (HREELS) was used to identify this surface intermediate as the asymmetric structure shown in Scheme 1, namely a surface oxametallacycle.[4] This work

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provided important evidence that the surface oxametallacycle can react on the Ag surface to form EO, which is consistent with the hypothesis that sequential formation of C–O bonds is the dominant pathway in ethylene epoxidation. Subsequent theoretical and microkinetic modeling studies have bolstered the conclusion that the surface oxametallacycle is the key intermediate in this process.[5–8] The surface oxametallacycle was identified on the basis of the vibrational fingerprint obtaind in experiments in which it was quite difficult, because of thermodynamic constraints, to obtain a high surface concentration of this intermediate and therefore a high-quality vibrational spectrum.[4] We have thus explored additional tools to conclusively identify the relevant surface intermediate. The identification of this intermediate is crucial, since many aspects of ethylene epoxidation, most importantly selectivity, are governed by the surface chemistry of the intermediate.[2,6,8] Also, a thorough understanding of the nature of C–O bond formation could have a significant impact on other epoxidation processes, such as the potential development of stable and efficient heterogeneous catalysts for propylene epoxidation.

Herein, surface intermediates formed upon adsorbing EO onto Ag(111) at various temperatures are examined by a combination of high-resolution X-ray photoelectron spectroscopy (HRXPS) and density functional theory (DFT). The work presented herein is significant not only because it reinforces the link between the existence of surface oxametallacycles and EO formation on Ag, but also because it represents a clear illustration of a potential utility of the combined use of HRXPS and DFT to investigate interesting surface intermediates by probing the electronic structures of atoms that form them. High-resolution chemical information obtained in HRXPS experiments is sufficient to conclusively identify intermediates and even to distinguish among those which are fairly similar.

Ethylene oxide was adsorbed onto a clean Ag(111) crystal at various adsorption temperatures and the C 1s X-ray photoelectron spectra were measured as a function of the adsorption temperature. Figure 1 shows the C 1s HRXPS spectrum after exposure of Ag(111) to EO at temperatures of 100 and 130 K. Measurements obtained after adsorption of EO at 100 K reveal that the ethylene oxide exists in two different states. The peak at 287.1 eV is assigned to multilayers of ethylene oxide, while the peak at 286.2 eV is assigned to molecular EO that is weakly bound to the surface. These assignments are corroborated by the observation that the peak at 287.1 eV corresponding to EO multilayers disappears after flash heating the sample to 157 K. It is also observed that the weakly bound molecular EO is almost completely desorbed after flash heating the sample to 204 K. Figure 1 also shows the C 1s HRXPS spectrum after EO was adsorbed onto Ag(111) at 130 K. It is observed that at this temperature the adsorbate is the weakly bound molecular EO, as indicated by the peak at 286.2 eV. This species desorbed after the sample was flash heated to 202 K, as evidenced by the disappearance of the C 1s peak. Peak-fitting of the HRXPS spectra after low-temperature adsorption of EO also indicated that the two C atoms are chemically indistinguishable in molecularly adsorbed EO, that is, the symmetric framework of the EO molecule is preserved.

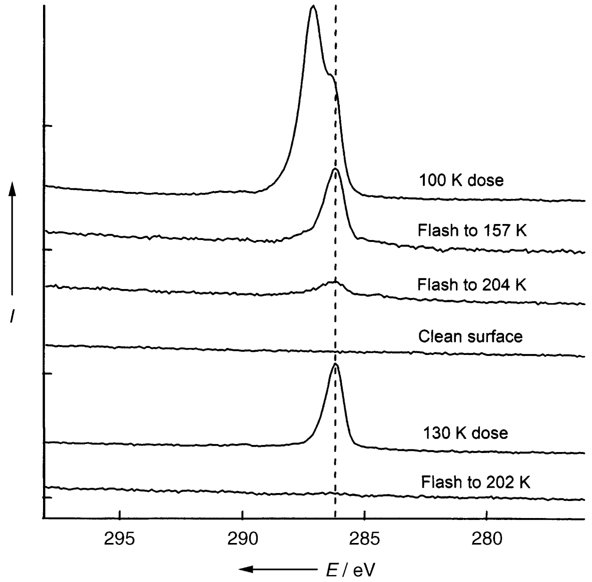

Figure 1. Measured C 1s spectra after EO was adsorbed onto the Ag(111) crystal plane at 100 K or 130 K, and subsequently heated to the temperatures indicated. States corresponding to multilayers and molecularly adsorbed EO are observed.

In separate experiments, EO was adsorbed onto the Ag(111) surface at 225 and 250 K. The corresponding C 1s HRXPS spectra are shown in Figure 2. The spectrum measured after adsorption of EO at 225 K is characterized by two peaks. One peak is centered at 286.5 eV and assigned to weakly bound molecular EO. It is observed that there is a

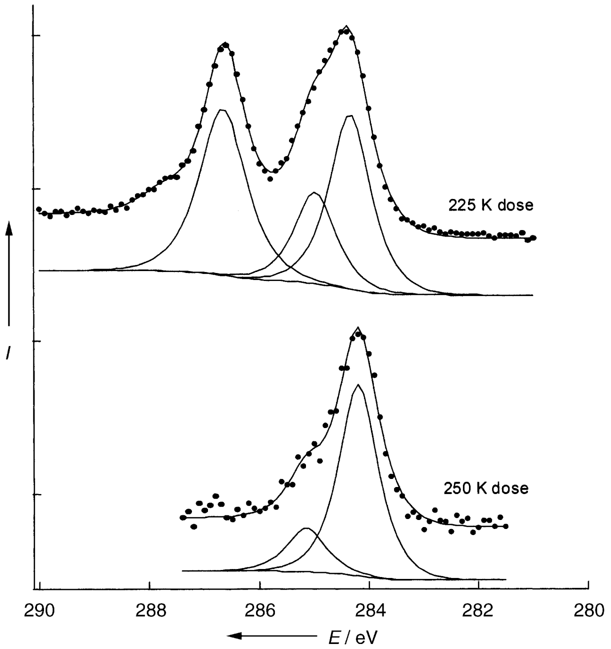

Figure 2. Measured C 1s spectra after EO was adsorbed onto the Ag(111) crystal plane at 225 K or 250 K. The lower lines represent peak-fits to the measured spectra. Multiple states are observed.

slight shift (from 286.2 to 286.5 eV) in the binding energy of the C 1s state compared to that in the low-temperature adsorption. This shift is a consequence of variation in the adsorbate coverage as a function of adsorption temperature and also a result of a different binding environment; molecular EO is not the only species present on the surface. The two effects lead to a change in the surface work function which becomes evident as a small shift in the binding energy. The adlayer adsorbed at 225 K is also characterized by an additional peak at lower binding energy (284.3 eV) that was not observed after adsorption at lower temperatures. The C 1s spectrum indicates that the species associated with this peak is chemically different from molecular EO. Furthermore, the peak-fit of the 284.3 eV peak suggests that there are two distinct carbon atoms contributing to the signal in this region, that is, an asymmetric surface intermediate is formed. The spectrum measured after EO was adsorbed at 250 K is characterized by only a broad peak in the 284–285 eV region corresponding to an intermediate with two distinct carbon atoms ; the peak at 286.5 eV assigned to molecular EO is not observed. It is important to reiterate that the intermediate formed on Ag(111) after adsorption of EO at 250 K reacts at 310 K to reform EO, as shown in TPD experiments.[4] The formation of this intermediate is an activated process—it does not occur for adsorption at 100–130 K, as demonstrated by the results of Figure 1 and previous TPD experiments.[4] We utilize below computational tools, mainly DFT, to assign the spectra shown in Figure 2 to a particular species on the surface.

When comparing experimentally measured electronic spectra to theoretical predictions from DFT it is often fruitful to focus on shifts in electron binding energies with respect to the binding energy of some standard.[9] In these experiments we have used the C 1s state of molecular EO as a standard. We are interested in shifts in the C 1s states as EO reacts to form a stable surface intermediate after it is adsorbed onto Ag(111) at approximately 250 K. The intermediate that has been proposed on the basis of its vibrational spectrum[4] is the surface oxametallacycle shown in Scheme 1.[4–7,10,11] The presence of two distinct carbon atoms in the asymmetric surface oxametallacycle structure is consistent with the peak-fit of the 284.3 eV HRXPS peak in Figure 2.

Figure 3a shows the experimental HRXPS spectra after adsorption of EO at 225 K onto the Ag(111) surface with energies shifted to utilize the C 1s peak of molecularly adsorbed EO as a reference. All-electron DFT calculations have been used to calculate the energy levels of the C 1s electrons in molecular EO and the surface oxametallacycle. The calculations were performed with only initial state effects,[12] that is, the reported energies represent the energies needed to remove electrons from the Kohn–Sham eigenvalues of the particular core state, the C 1s orbital. These calculations were done for the geometry of the surface oxametallacycle that was computed to be stable on a Ag_{15} cluster. The identical geometry was computed in pseudo-potential plane-wave calculations with the slab representation of the Ag(111) surface.[5,6] The peak shapes are simulated by assuming a Gaussian distribution with standard deviation values and peak heights measured in the experimental studies. The agreement between the experimental results and the theoretical predictions of C 1s chemical shifts is quite remarkable (Figure 3).

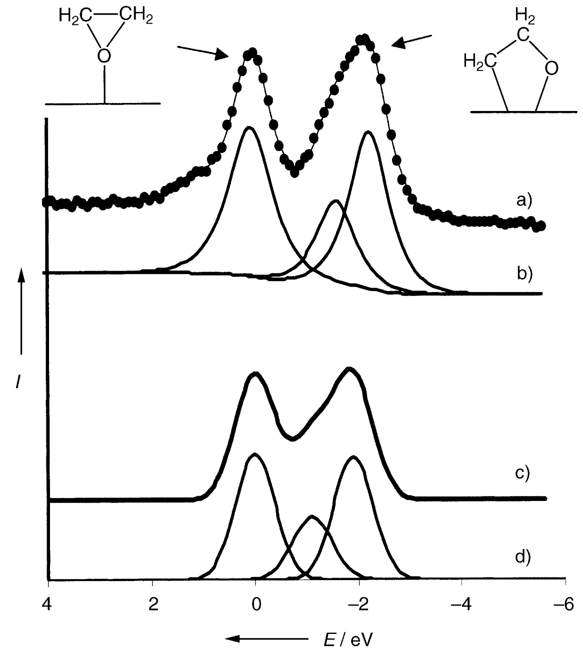

Figure 3. a) Measured C 1s spectra after EO was adsorbed onto the Ag(111) crystal plane at 225 K. The energy of 0 eV is assigned to molecular EO. b) Peak-fit for the measured spectrum. c) DFT-predicted C 1s spectra calculated from electronic structure calculations of EO and the surface oxametallacycle. This spectrum is computed as a superposition of the calculated C 1s peaks, shown in (d). d) DFT-calculated C 1s spectra for carbon atoms of molecular EO and the surface oxametallacycle. Experimental peak widths and heights are used.

From these experimental and theoretical studies it is concluded that after adsorption of EO onto the Ag(111) surface at 225 K there are two adsorbate states on the surface: weakly bound molecular EO and the surface oxametallacycle formed by opening of the EO ring. As the adsorption temperature is increased to 250 K the only species that remains on the surface is the oxametallacycle. The measured C 1s XPS spectrum of the surface oxametallacycle and chemisorbed EO are characterized by C 1s binding energies lower than those of physisorbed EO. The directions of these shifts are not surprising and are a probable consequence of charge transfer at the adsorbate. This process is driven by an alignment of the adsorbate electronic states with respect to the Fermi level of the substrate. It is also observed that the C 1s spectrum of the surface oxametallacycle formed after adsorption of EO at 250 K is characterized by peaks that are at lower binding energies than peaks assigned to molecular EO. This shift is measured to be approximately 1.5 eV for the central carbon atom of the oxametallacycle and approximately 2.3 eV for the terminal carbon atom. These shifts are calculated in DFT calculations to be 1.1 and 1.9 eV for the respective carbon atoms (Figure 3). The shifts for the surface oxametallacycle can be explained in terms of atomic charge distributions in the adsorbates. Even though the assignment of atomic charge is somewhat arbitrary, both Vernoi and

Mulliken analysis of the charge distribution illustrate that the C atoms of the surface oxametallacycle are less negatively charged that C atoms of molecular EO. The higher binding energies of the C 1s eigenvalues assigned to molecular EO compared to the surface oxametallacycle are a consequence of the extra Coulombic interactions between C 1s electrons and the ion cores of its more positively charged C atoms.

Ethylene oxide adsorbed on Ag(111) at 200–250 K undergoes ring opening to produce a stable surface intermediate. The experimental and theoretical studies on the electronic structure of the intermediate support the identification of this species as an oxametallacycle. This intermediate reacts at about 310 K to reform EO,[4] thus providing an important link between ethylene epoxidation on Ag and the surface oxametallacycle. The combination of HRXPS and DFT calculations to probe electronic structures of adsorbates permits the identification of important surface intermediates, including elusive species such as the oxametallacycle, to an unprecedented level of detail.

Experimental Section

High-resolution X-ray photoelectron spectroscopy (HRXPS) experiments were performed in a UHV chamber on the U12A beamline at the Brookhaven National Laboratory. The chamber was equipped with turbo-molecular and cryo pumps. This pumping system was able to achieve base pressures of 1×10^{-10} Torr. The chamber was also equipped with a UTI 100C mass spectrometer for TPD experiments. XPS spectra were collected in the fixed pass energy mode using a concentric hemispherical analyzer. The setup allowed for resolution better than 0.3 eV. Binding energies were calibrated by setting the instrument work function to fit the position of the $Ag3d_{5/2}$ line, which was used as a standard.

The Ag(111) single crystal was mounted on a 0.25 mm Ta wire loop which was spot-welded to two additional Ta wires. The sample could be resistively heated to over 900 K or cooled to 110 K by controlling the temperature of two Ta wires to which the sample was attached. The sample temperature was monitored by a K-type thermocouple spot-welded to the Ta wire loop. The sample was cleaned by successive cycles of Ar ion bombardment followed by annealing at 900 K. The surface cleanliness was confirmed by the absence of O 1s and C 1s signals in the XPS spectrum.

The EO used in the experiments (99 %, Aldrich) was transferred to the chamber from a lecture bottle through a short stainless-steel tube. Dosing was accomplished in a direct fashion by bringing the Ag single crystal to a distance of about 1 cm from the outlet of the stainless-steel tube.

The Amsterdam density functional (ADF) program was implemented to calculate fully optimized geometries of molecular gaseous EO and surface oxametallacycles adsorbed on Ag_{15} clusters, as previously described.[6] The same program was used to calculate the energetic positions of C 1s orbitals in these structures. The program represents molecular orbitals as linear combinations of Slater-type atomic orbitals. All calculations were spin-unrestricted and employ Becke[13] and Perdew[14] gradient approximations for the exchange and correlation energies, respectively. Double-zeta basis sets with polarization were employed in all computations.

The XPS spectra were calculated assuming that the binding energy "seen" by the photoelectron leaving a core level is identical to that before ionization, hence all other electrons are in the same state before and after the photoionization event. Possible relaxation effects are not taken into account.[12] This assumption means that the screening contribution from the valance electrons in the response to a created hole is identical for excitation from both C 1s states and that the electron self-interactions are identical for both respective electrons.

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