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Formation of a Stable Surface Oxametallacycle that Produces Ethylene Oxide

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Abstract: Temperature programmed desorption, high-resolution electron energy loss spectroscopy (HREELS), and density functional theory (DFT) were used to investigate the adsorption and reaction of ethylene oxide (EO) on the Ag(111) surface. When EO is dosed onto Ag(111) at 140 K it adsorbs molecularly, desorbing without reaction at ~200 K. On the other hand, when EO is dosed at 250 K, the ring-opening of EO is activated, and a stable surface intermediate is formed. This intermediate reacts at 300 K to re-form EO plus a few other products. HREELS and DFT studies suggest that this stable intermediate is a surface oxametallacycle. Moreover, the activation energies observed for the reaction of the oxametallacycle to form EO are in an excellent agreement with the values reported for the steady-state ethylene epoxidation process. This work represents the first demonstration of surface oxametallacycle ring-closure to form EO. Comparison of the spectroscopic results obtained from silver single crystals and supported catalysts strongly suggests that oxametallacycles are important intermediates in silver-catalyzed ethylene epoxidation.

Introduction

Ethylene oxide generated by ethylene epoxidation is among the largest volume chemicals produced by the chemical industry. The recent commercialization of a process that involves epoxidation of 1,3-butadiene to form 1-epoxy-3-butene (EpB) has focused increased attention on direct olefin epoxidation.[1] Both of these processes employ silver catalysts supported on α-Al_2O_3 and promoted by alkalis and halides.

Considerable effort has been devoted to understanding the mechanism of silver-catalyzed ethylene epoxidation.[2] The issues most often addressed have been the roles of oxygen and the promoters in the reaction. It is generally accepted that atomic, rather than molecular, adsorbed oxygen reacts with ethylene.[3] The same conclusion has been drawn for the epoxidation of styrene,[4] norbornene,[5] and 3,3-dimethylbutene.[6] Because of the rate-limiting nature of oxygen addition to the olefin and the fact that the subsequent steps are rapid, little has been learned about the nature of the organic intermediate(s) formed during these epoxidation reactions.

One species proposed as a possible intermediate, not only for olefin epoxidation but also in the reaction of various oxygenates on transition metal surfaces,[7-11] is the surface oxametallacycle. One version of this species, which contains an O−C−C backbone attached at both ends to the metal surface, has recently been isolated and spectroscopically identified in the reaction of 2-iodoethanol on Ag(110)[12] and Ag(111).[13] During temperature programmed desorption (TPD) experiments, this oxametallacycle reacted on Ag(110) to form γ-butyrolactone (GBL) and acetaldehyde as major products. No direct experimental link between the oxametallacycle and ethylene oxide was found. The first link between an oxametallacycle intermediate and an epoxide was established in the work of Medlin et al.[11] in which EpB was adsorbed on a Ag(110) crystal plane in ultrahigh vacuum (UHV) at 300 K, forming an oxametallacycle. This intermediate reacted at 500 K to re-form EpB plus 2,5-dihydrofuran. The activation energy measured for ring-opening EpB to form the oxametallacycle was 8 kcal/mol. The activation energy for ring-closure of the oxametallacycle to re-form EpB was 32 kcal/mol, in excellent agreement with the results of DFT calculations.[14]

As part of a continuing effort to understand the mechanism of olefin epoxidation, we have focused on investigating similar intermediates on Ag(111). Density functional theory (DFT) calculations have recently demonstrated that surface oxametallacycles are moderately stable with respect to the corresponding gas-phase monoolefin epoxides.[15,16] This observation not only indicates that oxametallacycles are energetically feasible

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intermediates for olefin epoxidation, but also suggests the possibility of ring-opening epoxides other than EpB on silver to form stable oxametallacycles. This idea is explored in this work through the reaction of EO on Ag(111). The adsorption of EO on silver surfaces in UHV has been probed by several investigators.[17−19] They found that upon adsorption of EO onto silver surfaces at liquid nitrogen temperatures, no reaction was observed. The unique approach of this work is that EO is adsorbed onto the Ag(111) crystal plane at various temperatures, anticipating that the ring-opening of EO would be activated and would lead to the formation of a stable intermediate. We have used temperature programmed desorption, high-resolution electron energy loss spectroscopy (HREELS), and density functional theory-based ab initio calculations to examine the adsorption and reaction of EO on the Ag(111) surface.

We report here isolation of an intermediate during the reaction of EO on Ag(111). This intermediate reacts to re-form EO and a few other products. The experimental and theoretical results described strongly suggest that this stable surface species is an oxametallacycle. We believe that this work represents another link between a stable oxametallacycle and a gas-phase epoxide. We provide experimental and theoretical vibrational spectra used to identify the oxametallacycle, as well as the possible reaction coordinate for oxametallacycle ring-closure to form EO. We also propose a reaction coordinate for the epoxidation of ethylene to form EO over silver catalysts.

Experimental Section

Experiments were performed in two UHV chambers. Temperature programmed desorption (TPD) experiments in the first chamber were carried out as described previously.[12] High-resolution electron energy loss (HREELS) experiments were performed in a second chamber, previously described.[20] The system was equipped with an LK Technologies ELS 300 spectrometer. All of the spectra were collected in the specular direction with the electron beam incident 60° to the surface normal. The electron beam energy was 3 eV with a full width at half maximum (fwhm) resolution of 30−35 cm^{-1} for the elastically scattered beam.

The silver single crystal was aligned to the (111) orientation by the Laue method, cut, and polished using standard metallographic techniques. The initial cleaning of the Ag(111) crystal was accomplished by cycles of argon ion bombardment followed by annealing to 950 K. The surface orientation and cleanliness were verified using LEED and HREELS, respectively. In both systems, the Ag(111) sample was mounted on a tantalum foil backing plate which was spot-welded to two tantalum wires. Sample heating was accomplished by passing a current through the wires. The EO used in the experiments (99% purity, Aldrich) was transferred to the chamber from a lecture bottle through a short stainless steel tube.

Computational Details

The Amsterdam density functional (ADF) program was implemented to calculate fully optimized geometries of EO oxametallacycles adsorbed on Ag clusters, as previously described.[15,16] The same program was used to calculate infrared spectra of optimized oxametallacycle structures. ADF is used to solve one-electron Kohn−Sham equations using the Vosko−Wilk−Nusair (VWN) functional.[21] The program represents molecular orbitals as linear combinations of Slater-type atomic orbitals. All calculations were spin-unrestricted and employ Becke[22]and Perdew[23] gradient approximations for the exchange and correlation energies, respectively. Double-ζ basis sets were employed in all computations.

Energies (stability values) for the formation of an oxametallacycle resulting from EO addition to a bare silver cluster were calculated as

$$\Delta H_{\mathrm{rxn}} \cong \Delta E_{\mathrm{rxn}} = E(\text{oxametallacycle}) - E(\text{EO}) - E(\text{cluster}) \quad (1)$$

where E(EO) and E(cluster) are total energies of gas-phase EO and the bare silver cluster, respectively.

The infrared spectrum of an oxametallacycle was calculated by carrying out two-point frequency calculations using an integration accuracy of 10^{-6}. The resulting frequencies are reported as calculated, without scaling.

Results

The results are presented in three sections. The first section describes temperature programmed desorption of EO on Ag(111). The HREELS data are reported in the second section, while the final section contains DFT calculations.

Temperature Programmed Desorption. Ethylene oxide adsorbed onto the clean Ag(111) surface at 130 K desorbs molecularly at 200 K. In Figure 1a we show the mass fragment $m/e = 29$ spectrum used to track EO. Variation of the EO exposure reveals that this peak saturates for larger doses, so it can be attributed to molecularly adsorbed EO. The desorption temperature of molecularly adsorbed EO is in agreement with the previous observations in similar experiments performed on Ag(110).[18,24,25] There is also a small feature in the TPD spectrum at 300 K; however, the intensity of this peak is too small to permit the identification of the desorbed products.

Figure 1b shows the spectrum of the $m/e = 29$ fragment after EO has been adsorbed onto the Ag(111) crystal plane at 250 K. We observe a much larger $m/e = 29$ peak at 300 K which is attributed to EO. It is important to note that the TPD experiments involved monitoring of 20 representative masses which provided a great level of confidence when ruling out products with similar fragmentation patterns, such as acetaldehyde. Figure 2 shows the corrected desorption spectra for the major products. The root-mean-square error associated with the product assignment was found to be approximately 3%. This value was determined by calculating the percent error between the experimental TPD peak areas and those expected for the assigned product distribution based on the fragmentation patterns for all 20 masses.

Increasing the EO exposure at 250 K results in an increase in the selectivity to EO to a value of 80% at saturation. Figure 3 shows the dependence of the selectivity to EO on the coverage. The EO exposure at 250 K required to saturate the 300 K peak was estimated to be of order 50 langmuirs (1 langmuir = 10^{-6} Torr s), assuming an enhancement factor of ca. 10 for the flux to the surface relative to the background pressure for direct dosing through the dosing tube. The saturation coverage of the 300 K peak following EO adsorption at 250 K is equivalent to the saturation coverage of molecularly adsorbed EO which desorbs at 200 K after EO adsorption at 130 K, shown in Figure

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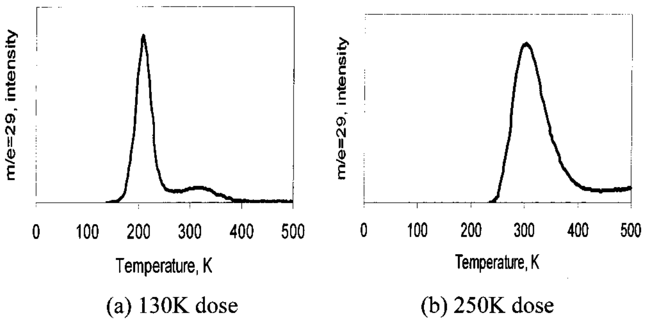

Figure 1. TPD spectra after EO dose to Ag(111). (a) $m/e = 29$ spectrum (used to track EO desorption) after 130 K dose; (b) corrected EO desorption spectrum after 250 K dose.

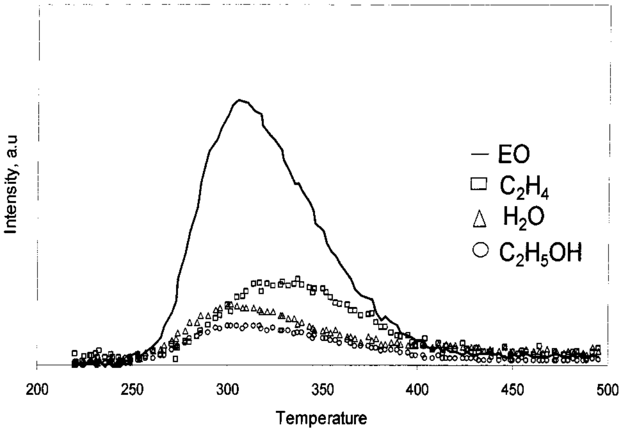

Figure 2. TPD spectra following a 250 K dose of EO on Ag(111).

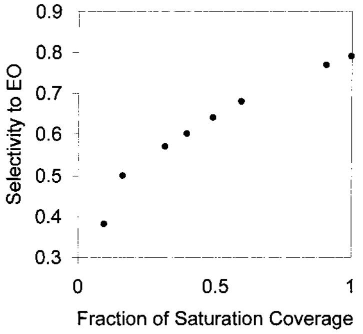

Figure 3. Selectivity to EO during TPD as a function of coverage of strongly bound intermediate, after 250 K dose.

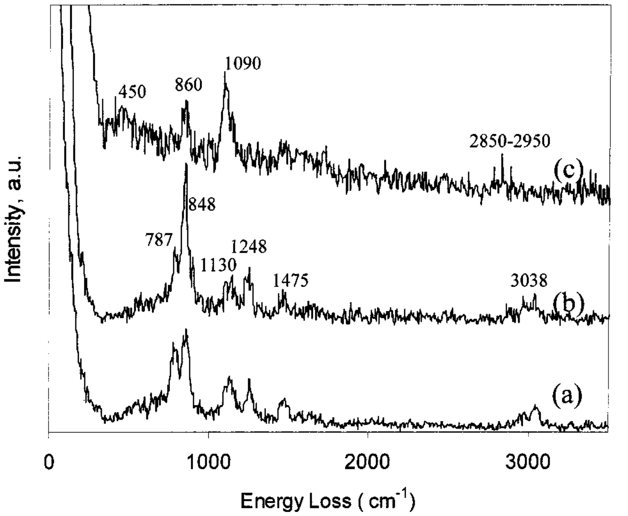

Figure 4. HREEL spectra collected after exposing EO to Ag(111) at varying dose temperatures. (a) 110 K; (b) 140 K; (c) 250 K.

1a. The results shown in Figures 1a,b, and 2 are indicative of the presence of a stable surface intermediate that is responsible for the reaction channel observed at 300 K. The dependence of the intensity of the 300 K peak on the adsorption temperature of EO indicates that there is a significant activation energy required for the formation of this surface intermediate. By analogy to the similar behavior observed for EpB, it is most likely that this activation energy is required for ring-opening of EO. The ring-opening of EO can be accomplished by the cleavage of either a C−C or a C−O bond. Cleavage of a C−C bond would almost certainly lead to the formation of products with only one carbon; no such products were observed in our experiments. On the other hand, the cleavage of a C−O bond would result in the formation of an intermediate that could subsequently react to re-form EO and to form other products with C−C bonds intact, consistent with the experimental observations. Determining the nature of this surface intermediate requires the use of surface spectroscopic techniques.

High-Resolution Electron Energy Loss Spectroscopy. To identify the intermediate involved in the reaction of EO on Ag(111), a series of HREELS experiments was performed. First, EO was adsorbed at 110 K and maintained at that temperature for HREELS analysis. The resulting spectrum is shown in Figure 4a. On the basis of comparison with reported IR spectra of the gas-phase EO, this spectrum is attributed to multilayers of EO. Figure 4b shows a spectrum collected after adsorbing EO onto the Ag(111) crystal plane at 140 K. As suggested by our TPD experiments and experiments performed by others,[18,24−26] this temperature is sufficiently high to prevent the formation of multilayers. Since this spectrum is just slightly perturbed from the one assigned to multilayers of EO, it can be concluded that the chemisorbed EO is weakly bonded to the Ag(111) surface. The observed frequencies are in an excellent agreement with those reported by Backx et al.[24] and Bare.[18] The assignments of the observed vibrational modes are listed in Table 1. A description of the normal modes was obtained by viewing the DFT-based predicted normal modes derived from the frequency calculations for the fully optimized geometry of the EO molecule. The DFT results and mode assignments are discussed in subsequent sections.

In a separate experiment, EO was adsorbed onto the Ag(111) surface at 250 K. After the excess EO was pumped out, the surface was cooled, and the temperature was maintained at 150 K for HREELS analysis. The collected spectrum is shown in Figure 4c. This spectrum is significantly different from the one assigned to molecularly adsorbed EO shown in Figure 4b and thus represents a new species that is chemically different from EO. This observation is in agreement with the TPD experiments in which molecularly adsorbed EO desorbed by 200 K. This new surface species reacted in TPD experiments to form EO and a few other products at 300 K. The analysis of the HREELS spectrum and its comparison to the DFT-calculated vibrational spectrum of an oxametallacycle intermediate suggest that the species isolated after dosing EO at 250 K is a surface oxametallacycle, as discussed in the subsequent section.

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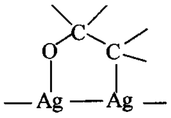
Table 1. Vibrational Mode Assignment of HREELS Frequencies (cm^{-1}) of Molecularly Adsorbed EO on Clean Ag(111)

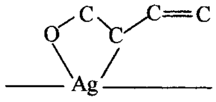
symmetry[a]	normal mode	IR gas[b]	IR liquid[c]	EO on Ag(111)	DFT prediction
A_1	ring deform	877	864	848	860
	CH_2 wag	1148	1124	1130	1105
	ring stretch	1270	1268	1248	1255
	CH_2 scissor	1498	1492	1475	1486
	CH_2 stretch	3018	3014	3007	3004
B_1	CH_2 rock	872	864	787	798
	CH_2 twist	1151	1150	1130	1125
	CH_2 stretch	3006	3003	2989	3101
B_2	ring deform	821	799	787	802
	CH_2 wag	1142	1150	1130	1110
	CH_2 scissor	1472	1468	1475	1455
	CH_2 stretch	3065	3072	3038	2998
A_2	CH_2 wag				1005[d]
	CH_2 twist				1128[d]
	CH_2 stretch				3086[d]

[a] Irreducible representation corresponding to C_{2v} symmetry of gaseous EO. [b] From ref 27. [c] From ref 28. [d] The intensity associated with this frequency is zero.

Density Functional Theory Calculations. This work continues our use of first principles DFT calculations as a complementary technique to TPD and HREELS experiments to identify important surface intermediates. Oxametallacycles have been proposed as surface intermediates in numerous reactions[7−10] but so far they have been spectroscopically identified on a surface only a few times. The first stable and spectroscopically identifiable oxametallacycle was observed in the reaction of 2-iodoethanol on Ag(110).[12] The structure of this oxametallacycle is shown below.

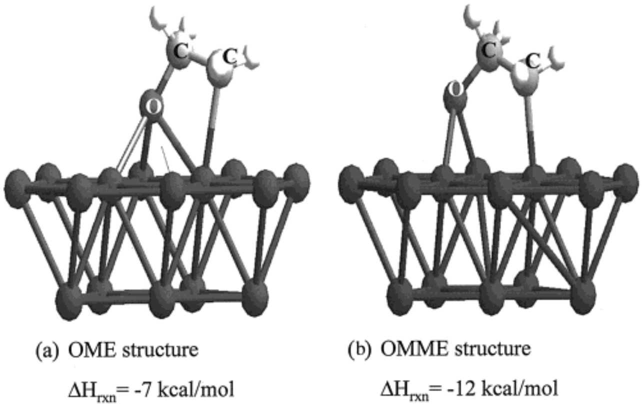


This structure incorporates two metal atoms in a five-membered ring with a backbone O−C−C linkage. Because there are two metal atoms that are part of the oxametallacycle ring, it is referred to as the OMME structure. The second identified oxametallacycle was observed in the reaction of 1-epoxy-3-butene (EpB) on Ag(110).[11] This oxametallacycle was structurally different from the one derived from 2-iodoethanol since it had a single metal atom incorporated in a four-membered ring.



We refer to this oxametallacycle structure as the OME structure. Previous investigations[15,16] suggest that OMME and OME structures are sufficiently energetically similar that theory alone is unlikely to determine definitively which would be formed. Thus surface spectroscopic methods are necessary to determine which type of oxametallacycle intermediate, if any, is formed.

An oxametallacycle can be formed conceptually in the reaction of EO on Ag(111) by the cleavage of a C−O bond and the insertion of one or two Ag atoms to form a four- or five-membered ring, respectively. The initial DFT calculations consisted of finding optimized geometries for these two possible structures. The calculations were performed for a few different size clusters. It was concluded that there was no significant change in the oxametallacycle stabilities (defined in eq 1) for the clusters larger than Ag_{15}. Figure 5 shows the optimized, energetically most stable, structure for the OME and OMME structures on an Ag_{15} cluster. Stability values for each oxametallacycle are also reported. It is concluded that the OMME structure with oxygen occupying a bridge site is modestly more stable than the OME structure with oxygen residing in a 3-fold hollow site. However, this energetic difference is not sufficient to rule out the OME structure.



(a) OME structure

ΔH_{rxn}= -7 kcal/mol

(b) OMME structure

ΔH_{rxn}= -12 kcal/mol

Figure 5. Optimized structures of EO oxametallacycles. (a) OME structure; (b) OMME structure.

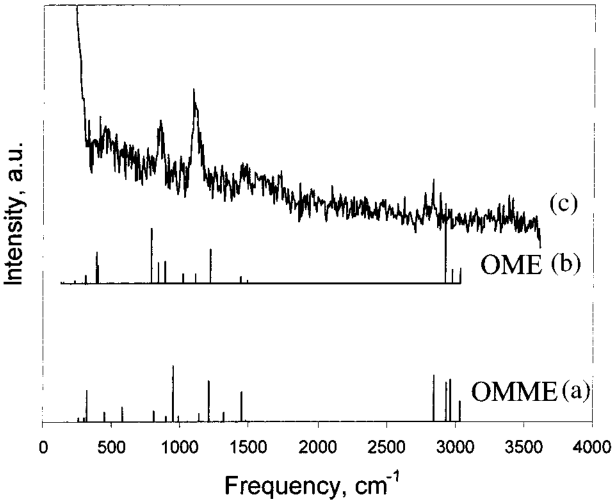


Figure 6. Calculated IR vibrational spectra of oxametallacycles on an Ag_3 cluster. (a) OMME structure; (b) OME structure; (c) HREEL spectrum of the surface intermediate.

To obtain a first approximation of the vibrational spectra of the EO oxametallacycles, frequency calculations were performed on Ag_3 clusters, with geometries of the cluster consistent with the Ag(111) crystallographic orientation, where the oxametallacycle geometries remained the same as the ones calculated on Ag_{15} clusters shown in Figure 5. Similar calculations were subsequently performed on the larger clusters, and no significant changes in the frequencies were observed. This is consistent with our previous findings.[12] In Figure 6 we report the computed IR spectra calculated on Ag_3 clusters for the OME and OMME structures and compare these to the experimental HREEL spectrum of the surface intermediate. It is important to note that the computed spectra are actually IR spectra, but since the dipole selection rules for IR and HREELS are the same, it is

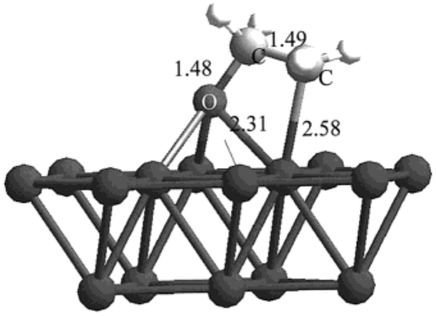


Figure 7. Structure of optimized EO oxametallacycle on a 15-atom Ag(111) cluster. Bond distances are indicated in angstroms.

Table 2. Vibrational Modes of Oxametallacycle Intermediate

normal mode	HREELS, intermediate on Ag(111)	DFT-predicted, OME frequencies
ring deform (C−C−O)	450	408
ring deform (C−O)		790
CH_2 rock	860	840
CH_2 rock		881
ring deform (C−C)	1090	1020
CH_2 wag		1090
CH_2 wag (parallel to surface)		1220
CH_2 scissor	1475	1432
CH_2 scissor		1484
CH_2 stretch	2850−2950	2900−3000

[a] DFT-predicted modes are calculated on Ag_{15}; frequences are in cm^{-1}.

reasonable to compare these, as we have shown previously.[12] By comparing the calculated spectra to the HREEL spectrum obtained after EO was adsorbed onto Ag(111) at 250 K, shown in Figures 3 and 6, it should be possible to determine which oxametallacycle geometry best corresponds to the structure of the surface intermediate. We conclude that the OME is the preferred structure since the computed spectrum for this structure more closely resembles the HREEL spectrum of the surface intermediate. In general, there is good agreement between observed HREELS frequencies and IR frequencies calculated for the OME geometry. The major modes are accurately predicted by the theory. There are predicted sets of bands at 850 cm^{-1} and at 1090 cm^{-1}, both consistent with the HREELS observations. The weak modes that appear at 1490 and 2900 cm^{-1} in the measured spectrum are also accurately predicted. The only peak that is predicted by theory but does not appear in the HREELS spectrum is at 1225 cm^{-1}. Upon careful examination of the dynamic dipole moment that is created by the normal mode responsible for the predicted peak at 1225 cm^{-1}, it was concluded that this dipole moment is parallel to the surface. Thus in HREELS experiments it is subject to the surface dipole-scattering selection rule which is not captured in the theoretical spectrum. This rule states that any normal mode with its dynamic dipole parallel to the metal surface will not be seen by dipole scattering. This is a consequence of the formation of an equally intense but oppositely directed mirror image dipole in the surface. It is important to recognize that the same selection rule suggests the need to place the main emphasis on comparing the frequencies of measured and calculated vibrational modes, rather than comparing their intensities.

DFT calculations were also performed for the OME structure on a Ag_{15} cluster, the structure of which is shown in Figure 7. The calculated IR spectrum is compared to the measured HREEL spectrum of the stable surface intermediate isolated at 250 K. Table 2 lists the IR frequencies calculated using DFT, along with the experimental HREELS frequencies. The energy losses at 850, 1090, 1490, and around 2900 cm^{-1} are predicted well. The agreement between the theoretical and experimental spectra suggests that the isolated intermediate is indeed an oxametallacycle in the OME conformation.

Vibrational Mode Assignments. As stated in the previous sections, complete animations of the calculated normal modes allow us to assign each frequency that appears in the HREELS spectrum to the corresponding normal mode. Tables 1 and 2 report only a simplified description of each normal mode; however, these vibrational modes are much more involved and are usually characterized by simultaneous motions of several atoms in a molecule. More detailed descriptions of the normal modes of molecularly absorbed EO and the oxametallacycle intermediate are provided here.

As shown in Table 1, the DFT-predicted vibrational spectrum for gas-phase EO is consistent with both the HREEL spectrum for molecularly adsorbed EO on Ag(111) and the IR spectrum of gas[27] and liquid[28] EO. The observed energy losses at 787 and 848 cm^{-1} are attributed to the CH_2 rocking mode and symmetric EO ring deformations, respectively. The band of peaks in HREELS experiments that is centered at 1130 cm^{-1} is attributed to CH_2 wagging modes. The calculated DFT spectrum suggests that there are four different CH_2 wagging modes, one of which, with A_2 symmetry, vanishes due to the dipole selection rules. The CH_2 wagging modes are very close in frequency, so it is impossible to resolve them in HREELS experiments. The normal mode observed at 1248 cm^{-1} is theoretically predicted at 1255 cm^{-1} and is attributed to a COC ring breathing mode. The mode observed in HREELS experiments at 1475 cm^{-1} can be described as a CH_2 scissor. These modes are well predicted by DFT-based frequency calculations as a doublet appearing at 1423 and 1456 cm^{-1}. Finally, the higher frequency peaks centered around 3000 cm^{-1} correspond to various symmetric and asymmetric stretches of C−H bonds. DFT predicts four slightly different frequencies corresponding to four different normal modes. Due to technique limitations, it is not possible to resolve this band of peaks in HREELS. It is concluded that every feature observed in HREELS can be accounted for by the theoretical predictions for the IR spectrum of EO. This excellent agreement between experiment and theory conclusively identifies the species isolated after EO adsorption at 140 K as molecularly adsorbed EO that is little perturbed by its interaction with the surface. It can also be concluded that the C_{2v} symmetry of gas-phase EO appears to be preserved for the adsorbed molecule.

Table 2 lists the HREELS frequencies after dosing EO onto the Ag(111) crystal plane at 250 K and the DFT-predicted frequencies for the OME oxametallacycle on a Ag_{15} cluster. The lowest frequency observed in the HREEL spectrum is centered around 450 cm^{-1}; this peak is also observed in DFT calculations at 408 cm^{-1}. This frequency is assigned to a ring deformation mode in which oxygen and carbon approach each

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other in a way that suggests a possible reaction coordinate for oxametallacycle ring-closure to form EO. The band centered at 860 cm^{-1} is well predicted by 790, 840, and 881 cm^{-1} peaks. These modes are assigned to oxametallacycle ring deformation dominated by C−O stretch and CH_2 rocking modes. The mode observed at 1090 cm^{-1} is predicted by DFT as a ring deformation dominated by C−C stretch and CH_2 wag motions appearing at 1020 and 1090 cm^{-1}, respectively. These peaks are closely spaced so they are not resolved in HREELS experiments. Another band of peaks is seen in the HREEL spectrum around 1475 cm^{-1}. This band corresponds to CH_2 scissor modes predicted by DFT at 1432 and 1484 cm^{-1}. The higher frequency energy losses at approximately 2900 cm^{-1} are assigned to various C−H stretches. Nearly all of the energy losses observed in the HREELS spectrum are consistent with the predictions of DFT-based IR frequency calculations, identifying the stable surface intermediate as an oxametallacycle.

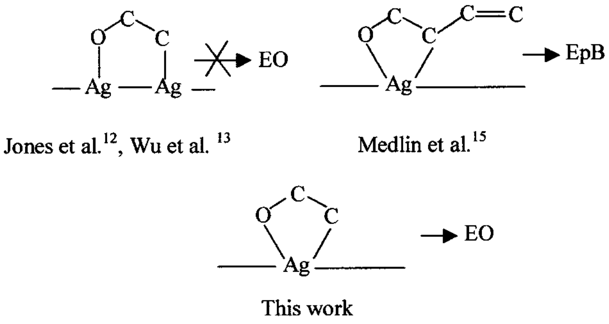
Discussion

The following discussion concentrates on a few major conclusions of this work. First, the fact that the energetically less preferable OME structure appears to be the surface intermediate rather than the OMME structure will be addressed. The link between the oxametallacycle structure and the selectivity to different products is discussed. Second, the adsorption and reaction of EO on the Ag(111) surface is compared to previous studies of the reactions of epoxides on metal surfaces. Finally, the parallels between the results of this work and the observations made in steady-state ethylene epoxidation are discussed.

As stated in the previous sections, the OME structure was found to be the surface intermediate responsible for the epoxide formation reaction that takes place at 300 K. It is somewhat surprising that the energetically preferred OMME structure was not identified on the surface. There are a few possible explanations for this observation. The first and most obvious reason for this is that there might be a significantly higher activation barrier in ring-opening EO to form the OMME structure versus the OME structure. This would suggest that the process of oxametallacycle formation by adsorption of EO on Ag(111) is dominated by kinetics rather than by thermodynamics. The second possibility is that the difference in stability between the OME and OMME structures, about 5 kcal/mol, is not enough to overcome additional effects. For example, the system is modeled in the DFT-based calculations as an independent oxametallacycle interacting only with the silver cluster. It would be expected that there would be certain interactions among oxametallacycles. If these interactions were taken into account, it is quite possible that the structure that occupies less space, the OME structure in this case, would be preferred on a crowded surface. This is consistent with the observations that the selectivity for EO formation at 300 K increases with increasing surface coverage.

It is also important to compare the findings of this work with the previously observed reactions of different oxametallacycles. In the previous cases in which oxametallacycles were isolated on Ag(110), the OME structure reacted to form an epoxide, while in the reaction of the OMME structure, no epoxide was formed.

This collection of observations suggests that the OME structure is required to close an oxametallacycle ring and form an epoxide. This is consistent with the mechanisms proposed in epoxide-forming reactions in homogeneous catalysis, where mononuclear metallaoxetane complexes, which are analogous to the OME rather than to the OMME structures, are proposed as intermediates.[29] To shed more light on the link between the OME structures and epoxides, reaction coordinate calculations were performed. By probing the potential energy hypersurface connecting the reactant and product species, we have located a possible transition state and computed an activation barrier for the reaction of the OME oxametallacycle structure to form EO, using the principles of transition state theory. Preliminary results suggest the geometry of this transition state on an Ag_{15} cluster shown in Figure 8. The activation energy for ring-closure from the OME intermediate is calculated to be 13 kcal/mol, which agrees reasonably well with the experimentally found value of 17 kcal/mol. The experimental value was calculated from the TPD data using the first-order Redhead analysis assuming a preexponential factor of 10^{13} s^{-1} and the experimental TPD heating rate of 1.8 K/s. On the basis of these calculations, a schematic reaction coordinate for the OME ring-closure to yield EO is proposed in Figure 9. The activation energies for EO formation calculated in this work are also compared with previous measurements in steady-state ethylene epoxidation in Table 3.



Although these observations support the hypothesis that the OME structure is needed for ring-closure, much remains to be learned about surface oxametallacycle chemistry. For example, the fact that the OMME structure isolated on Ag(110) after adsorption of 2-iodoethanol on the surface did not react to form EO, unlike the OME structure isolated on Ag(111) in this work, might be attributable to surface structural effects or to the presence of iodine during the reaction of the OMME structure on Ag(110). Whatever the cause of this difference, it is clear that oxametallacycles can react via several different pathways, strengthening the notion that these intermediates may be involved in a variety of surface reactions involving oxygenates.

The interaction of EO with single-crystal metal surfaces has drawn considerable attention within recent years. The adsorption and reaction of EO has been studied on Ag(110),[18,24,25] Ag(111),[17] and Cu(110)[30] as well as (111) surfaces of Pt, Pd, and Rh. These studies suggest that EO adsorbs on transition metal surfaces through the oxygen atom. The adsorbed EO desorbs from group IB metal surfaces without reaction at temperatures around 200 K. On the other hand, on group VIII metal surfaces EO undergoes a ring-opening process in which the C−O bond is cleaved. It has been suggested that the decomposition of EO on group VIII metal surfaces proceeds via an oxametallacycle

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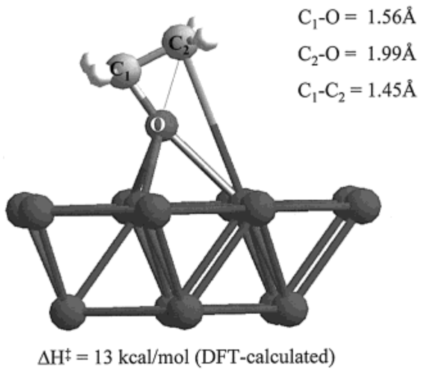

Figure 8. Structure of a possible transition state for reaction of the oxametallacycle to form EO. The bond lengths are indicated in angstroms.

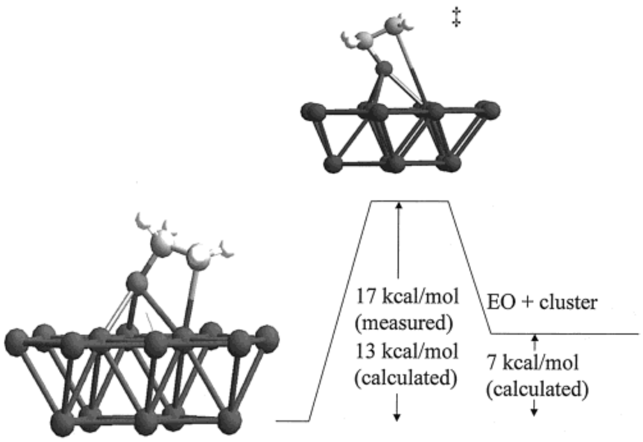

Figure 9. Schematic of the reaction coordinate for oxametallacycle ring-closure to yield EO. Activation barriers have been calculated from TPD results; the ΔH_{rxn} value is calculated for the EO oxametallacycle on a 15-atom Ag(111) cluster.

Table 3. Activation Energies for the Formation of EO

E_a (kcal/mol)	reference
17	TPD (this work)[a]
13	DFT (this work)[a]
22	33[b]
14	34[b]
17	35[b]

[a] Observed on Ag(111) in the reaction of the oxametallacycle to form EO. [b] Observed in the steady-state ethylene epoxidation process.

intermediate.[8] It is speculated that on reactive group VIII metal surfaces the oxametallacycle undergoes a rapid decomposition, making it very difficult to isolate and spectroscopically identify this intermediate. We have shown in this study that the EO ring-opening reaction can be activated on a group IB metal surface and that a stable oxametallacycle structure can be isolated if two requirements are fulfilled. The first requirement is that the C−O bond cleavage has to be activated during the adsorption. This means that EO should be dosed at temperatures that are sufficiently high to overcome the activation barrier for the EO ring-opening, but also sufficiently low to prevent a subsequent rapid decomposition of the oxametallacycle. In the case of EO on Ag(111), 250 K is an adequate dosing temperature. The other requirement is that the oxametallacycle isolated in this process must be more stable than the epoxide used to form it. This requirement stems from the principle of microscopic reversibility in which any elementary reaction requires the same transition state for forward and backward reactions. It is important to emphasize the role that quantum chemical calculations play in the process of finding a temperature window in which the adsorbate should be dosed. In this case, DFT was used not only to help us explain the experimental findings, but also to motivate the experiment itself by predicting the window of stability in which the oxametallacycle was, in fact, observed.

Table 4. Comparison of the Frequencies (cm^{-1}) Assigned to the Stable Surface Intermediate

HREELS (this work)[a]	DFT (this work)[b]	Force and Bell[c]
860	790, 840, 881	860
1090	1020, 1090	1080
1475	1432, 1484	
2850−3000	2900−3000	2820−2970

[a] After EO adsorption at 250 K on Ag(111). [b] DFT-calculated IR spectrum for the OME intermediate on Ag_{15}. [c] IR spectrum collected in a recirculation reactor.[31]

Because of its great industrial importance, the catalytic selective oxidation of ethylene to ethylene oxide has been investigated by many authors in steady-state continuous or batch processes. Here we compare previous observations with the conclusions of this study.

In a study of the infrared spectra of species present during the oxidation of ethylene in a batch recirculation reactor over a silica-supported silver catalyst, Force and Bell[31] proposed a mechanism in which it was suggested that a species with the IR spectrum presented in Table 4 was the intermediate in the formation of ethylene oxide. It has been suggested that silica strongly adsorbs IR at many regions of the spectrum which makes the collection of an IR spectrum over silica-supported metal catalysts extremely challenging.[32] However, the IR spectrum collected in the experiments performed by Force and Bell was obtained in a heated infrared cell which contained a silver-impregnated silica support and a pure silica disk. This setup allowed for collection of the spectrum of only those species adsorbed on the catalyst by subtracting out the spectrum of a pure silica disk and the other species present in the gas phase. As presented in Table 4, the IR spectrum of the intermediate observed by Force and Bell is very similar to the one observed in our HREELS studies, as well as the DFT-predicted spectrum for the oxametallacycle. This agreement supports the conclusion that the OME structure isolated in this work under UHV conditions on Ag(111) is relevant to the steady-state catalytic process as well.

Conclusions

Ethylene oxide adsorbed on Ag(111) at judicious temperatures undergoes ring-opening to produce a stable surface intermediate. The evidence presented in this work strongly suggests that this intermediate is a surface oxametallacycle. This oxametallacycle reacts at 300 K to re-form ethylene oxide and to form a few other products. The analysis of the normal modes assigned to the oxametallacycle suggests that there is a vibrational mode at about 400 cm^{-1} that appears to be a viable reaction coordinate for the oxametallacycle ring-closure to form EO. The DFT investigation of this reaction coordinate demonstrated that the

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activation energy required to form EO from the oxametallacycle is comparable to the activation energies reported in the steady-state ethylene epoxidation processes. The vibrational spectrum of the intermediate present on the surface upon the adsorption of EO onto Ag(111) at 250 K is quite similar to the vibrational spectrum of a species previously isolated and thought to be involved in catalytic ethylene epoxidation.[31]

This work presents the first demonstration of EO ring-opening on group IB metals under UHV conditions and the first evidence that the oxametallacycles may be actively involved in the process of ethylene epoxidation.

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