Spectroscopic studies of ethylene adsorption on oxygen-modified Ag(1 1 1) at high pressures

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Abstract

2-Iodoethanol adsorbs on Ag(1 1 1) to form 2-hydroxyethyl species which react at $\sim$230 K to eliminate water and ethylene and to deposit species of stoichiometry C_2H_4O. At high coverages, this forms predominantly oxametallacyclic species which exhibit vibrational modes at 759, 972 and 1069 cm^{-1}. The oxametallacycle thermally decomposes forming acetaldehyde. The reflection-absorption infrared spectra of both ethylene and ethylene oxide adsorbed on oxygen-activated Ag(1 1 1) at 300 K under a pressure of 1 Torr show that they react to form both acetaldehyde and ethylene oxide species. Ethylene oxide adsorbs at high pressures via the oxygen atom with the molecular plane tilted with respect to the (1 1 1) surface. All of the adsorbed ethylene oxide and the majority of the acetaldehyde desorb on heating to 390 K, with the remainder of the acetaldehyde being removed by heating to 450 K. These results are in accord with previous temperature-programmed desorption data which showed the formation of acetaldehyde, ethylene oxide and CO_2 in this temperature range. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The pathway to the catalytic formation of ethylene oxide from ethylene and oxygen has been extensively investigated over the past 20 years [1–4]. This work has shown that an Ag(1 1 1) single crystal provides a good model for the supported catalyst since it catalyzes the formation of ethylene oxide with kinetics that resemble those of supported catalysts [5–7]. It has also been demonstrated, using temperature-programmed desorption, that the active form of adsorbed oxygen for both selective and total oxidation is adsorbed atomic oxygen, not dioxygen species (see references therein [5,6]). Subsurface oxygen, which is also present during the reaction, is also proposed to be a spectator species, although this has been suggested to facilitate the nucleophilic addition of ethylene to adsorbed oxygen [5]. It was proposed in this work that the initial reaction between ethylene with adsorbed atomic oxygen formed total oxidation products (CO_2 and H_2O) and a surface precursor to ethylene oxide formation. The nature of the surface intermediate remains to be identified. There are two obvious candidates for this intermediate species. The first forms when both p-orbitals of the ethylenic π orbital simultaneously interact with adsorbed oxygen to form adsorbed ethylene oxide directly. This was suggested to be the intermediate formed in the work of Grant and Lambert, but with no supporting spectroscopic evidence. Alternatively, the p-orbitals

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can interact with both adsorbed atomic oxygen and the silver surface forming an oxametallacycle [9,10]. This would undergo a reductive elimination to form ethylene oxide. In the reaction pathway proposed by Grant and Lambert, the surface intermediate either reacts to form ethylene oxide or undergoes further oxidation to form CO_2 and H_2O. Such a double branching reaction pathway successfully accounts for the deuterium kinetics isotope effects found for this reaction [5,11,12].

This reaction pathway was elucidated based on measurements of the reaction kinetics and temperature-programmed desorption data following relatively large ethylene exposures ($\sim 10^7$ l, 1 l $= 1 \times 10^{-6}$ Torr s). The salient points of this work will be summarized below. In this work, the corresponding reflection-infrared spectra are collected, allowing the nature of the species present on the surface to be monitored and the reaction intermediates identified.

2. Experimental

The experiments were carried out in a stainless-steel, ultrahigh vacuum chamber operating at a base pressure of $\sim 8 \times 10^{-11}$ Torr following bakeout and which has been described in detail elsewhere [13]. Infrared data were collected from an Ag(1 1 1) single crystal sample mounted in a modified 2.75 in. six-way cross equipped with infrared-transparent, KBr windows. The sample could be resistively heated to 1000 K or cooled to 80 K using liquid nitrogen. Light from a Bruker Equinox infrared spectrometer passes through a polarizer and is focused onto the sample at an incidence angle of $\sim 80°$ and the reflected light steered onto the detector of a liquid-nitrogen-cooled, mercury–cadmium–telluride detector. The complete light path is enclosed and purged with dry, CO_2-free air. The spectrometer operated at $4 \, cm^{-1}$ resolution and data were typically collected for 2000 scans.

The infrared cell was attached to the main 12 in. diameter, ultrahigh vacuum chamber and the sample could be moved from the cell into the main chamber by means of a transfer rod. This chamber was equipped with a single-pass, cylindrical-mirror analyzer which was used to collect Auger spectra of the sample.

Temperature-programmed desorption data were collected using a heating rate of $\sim 3 \, K \, s^{-1}$ and desorbing

species detected using a Dycor quadrupole mass spectrometer located in the main ultrahigh vacuum chamber and interfaced to a PC allowing five masses to be monitored sequentially during the same desorption sweep.

The sample was cleaned using a standard procedure [14,15] which consisted of bombarding with Argon ions (1 keV, $2 \, \mu A \, cm^{-2}$) at 300 K and the annealing to 1000 K in vacuo to remove any remaining surface species. The ethylene oxide used for the experiments (Aldrich, 99% purity) was transferred to glass vials, attached to the gas-handling line of the vacuum system and further purified by repeated freeze-pump-thaw cycles and its cleanliness monitored mass spectroscopically. Ethylene (Matheson) was transferred from the cylinder to a glass bottle and further purified by bulb-bulb distillations and its purity verified mass spectroscopically. The 2-iodoethanol used for the experiments (Aldrich, 99% purity) was transferred to glass vials, attached to the gas-handling line of the vacuum system and further purified by repeated freeze-pump-thaw cycles and its cleanliness monitored mass spectroscopically. Perdeuteroethylene (C_2D_4) (Cambridge Isotopes, 98% D) was used as received. Normal oxygen ($^{16}O_2$) (Gas Tech, Inc.) was also transferred to a glass bottle and further purified by several freeze-pump-thaw cycles. Isotopically labeled oxygen ($^{18}O_2$) (Cambridge Isotopes, 98% ^{18}O) was used as received.

3. Results

3.1. Formation of oxametallacycles on Ag(1 1 1)

Fig. 1 shows a series of temperature-programmed desorption spectra collected following adsorption of 2-iodoethanol (3 l, 1 l $= 1 \times 10^{-6}$ Torr s) on Ag(1 1 1) at 80 K monitoring various masses. Exposures are not corrected for ionization gauge sensitivities. In addition, a series of experiments were performed with the sample biased to -100 V to prevent any electrons from the mass spectrometer ionizer (electron energy, 70 eV) from reaching the sample to test for electron-induced effects. The spectra collected in this way are identical to those without biasing the sample. In contrast to the behavior found on Ag(1 1 0), no γ-butyrolactone desorption is found [9,10]. Signals are found at all of
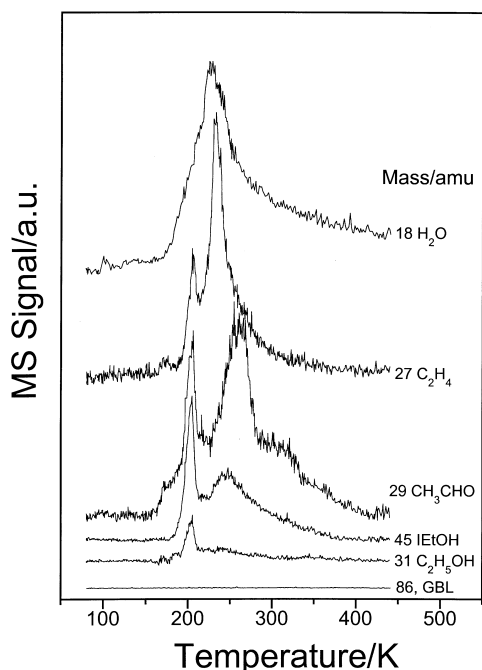
Fig. 1. Temperature-programmed desorption spectra of iodoethanol (31) adsorbed on Ag(1 1 1) at 80 K monitoring 18 amu (H_2O), 27 amu (ethylene), 29 amu (acetaldehyde), 45 amu (iodoethanol), 31 amu (ethanol) and 86 amu (γ-butyrolactone). The masses and the desorbing species are marked adjacent to the corresponding spectrum.

the other masses (18, 27, 29, 45 and 31 amu). All of the spectra (except that at 18 amu) exhibit a relatively sharp peak at 205 K. This peak increases in intensity with increasing iodoethanol exposure without saturating and is assigned to multilayer desorption. Similar multilayer desorption was found at a slightly higher temperature (225 K) on Ag(1 1 0) [9]. In addition, the relative intensities at each mass correspond well to the mass spectrometer ionizer fragmentation pattern of iodoethanol in agreement with this conclusion. Both water and ethylene desorb simultaneously in a relatively broad peak centered at ∼230 K suggesting that they are formed by the same reaction. The water desorption peak is slightly broader than that for ethylene which may reflect the slower pumping speed for the former molecule. A small amount of iodoethanol (45 amu) desorbs from the adsorbed overlayer at 245 K, in contrast to the behavior on Ag(1 1 0) where no molecular desorption was detected, except when multilayers had formed. Essentially no ethanol

(31 amu) desorption is detected since the 205 K peak in the spectrum collected at this mass is due to iodoethanol fragmentation. Two 29 amu states are detected at 260 and 315 K where, at this exposure, the 260 K feature is significantly more intense than that at 315 K. This contrasts the behavior on Ag(1 1 0) where the 29 amu signal was detected simultaneously with ethylene and water in two states at ∼340 and 263 K [9]. Note that both ethylene oxide and acetaldehyde have significant mass spectrometer ionizer fragments at 29 amu. However, the 29 amu species was unequivocally identified as acetaldehyde, not ethylene oxide, by carefully measuring the mass spectrometer ionizer fragments for acetaldehyde and ethylene oxide at various masses and comparing these with the temperature-programmed desorption spectra taken at these masses. Note that acetaldehyde desorbs from Ag(1 1 1) at substantially lower temperatures (160 K, [16]) so that the desorption states measured here represent a reaction- rather than desorption-rate-limited processes. Finally, no other higher molecular weight species, in particular due to γ-butyrolactone (Fig. 1), which was found on Ag(1 1 0) [9], were detected.

Fig. 2 shows the evolution of the 29 amu desorption spectra with exposure where the exposures in Langmuirs are marked adjacent to the corresponding spectra. Note that the sharp peak at 205 K for exposures larger than 2 l are due to the desorption of iodoethanol multilayers as discussed above. At low exposures (∼1 l), both the low- and high-temperature acetaldehyde desorption states are evident with relatively equal intensities. The high-temperature (315 K) state saturates at an exposure of ∼1 l whereas the low-temperature (235–260 K) state continues to grow with increasing exposure. In addition, the peak temperature of the low-temperature state increases slightly with increasing exposure so that at low exposures (0.5 l) it is centered at ∼235 K and shifts monotonically to higher values with increasing temperature, so is at ∼260 K for exposures of 2 l and greater. This effect may be due to the influence of some co-adsorbed iodoethanol and has been observed by others [17].

The corresponding exposure effect on the ethylene (27 amu) desorption profile is shown in Fig. 3 where again the 205 K feature that appears at larger exposures is due to multilayer iodoethanol desorption. Two peaks are seen at low exposures (0.5 l) at 205 and 225 K. The high-temperature peak of a similar two-peaked
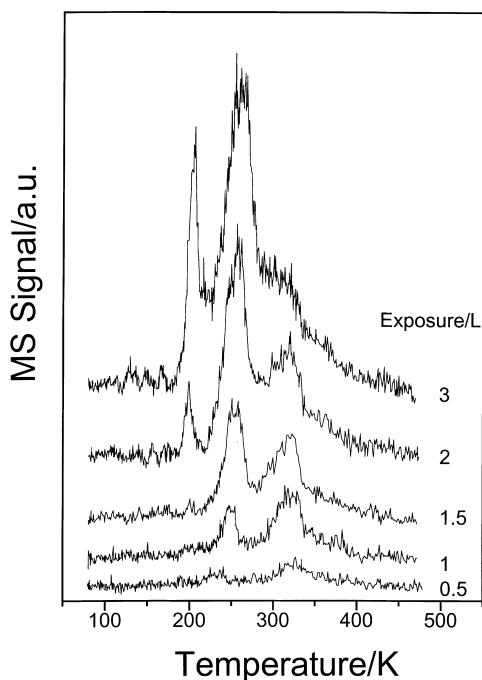
Fig. 2. Acetaldehyde (29 amu) temperature-programmed desorption spectra collected as a function of iodoethanol exposure at 80 K. The exposures (in Langmuirs) are marked adjacent to the corresponding spectra.
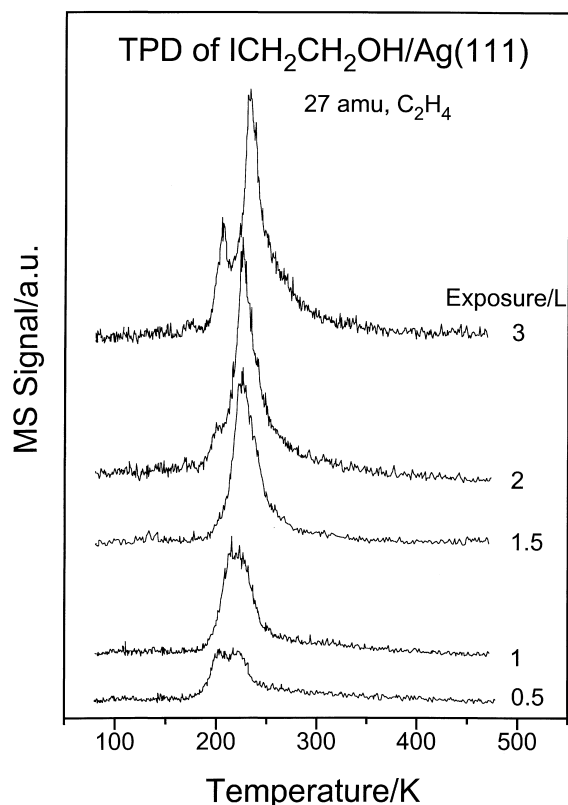

Fig. 3. Ethylene (27 amu) temperature-programmed desorption spectra collected as a function of iodoethanol exposure at 80 K. The exposures (in Langmuirs) are marked adjacent to the corresponding spectra.

spectrum on Ag(1 1 0) was ascribed to the effect of surface defects [8]. The ethylene desorption yield and peak temperature increase with increasing exposure, the peak temperature varying from 205 K at low exposures (0.5 l) to 230 K at high (3 l).

The desorption spectra for iodoethanol (45 amu) are displayed as a function of exposure in Fig. 4 where the growth of the multilayer (205 K) feature is clearly evident. A peak also appears at 245 K due to the desorption of iodoethanol adsorbed on the (1 1 1) surface. A Redhead analysis of the desorption state [18], assuming a pre-exponential factor of $1 \times 10^{13} \, s^{-1}$, yields a desorption activation energy for this state of $\sim$63 kJ mol^{-1}.

The relative molar desorption yields for ethylene, water and acetaldehyde are plotted as a function of iodoethanol exposure in Fig. 5. In this case, desorption yields are calculated from the integrated intensity under the desorption profile. This yield is converted to relative molar quantities by measuring the intensity at each of the masses detected in the desorption

spectra (29 amu for acetaldehyde, 27 amu for ethylene and 18 amu for water) for known pressures of each of these gases. These pressures were corrected for ionization gauge sensitivities. It is clear from these data that essentially equimolar amounts of ethylene, water and acetaldehyde are evolved for all iodoethanol exposures. Similar results were obtained for iodoethanol adsorbed on Ag(1 1 0) where equimolar amounts of water and ethylene desorbed both in the 263 and 340 K desorption states [9]. However, in contrast to the results obtained here on Ag(1 1 1), approximately 2 mol of acetaldehyde were formed for each mole of water or ethylene on Ag(1 1 0).

The RAIRS spectra associated with these desorption data have been collected and the results are summarized in Table 1. Their assignments have been discussed in greater detail elsewhere [19].
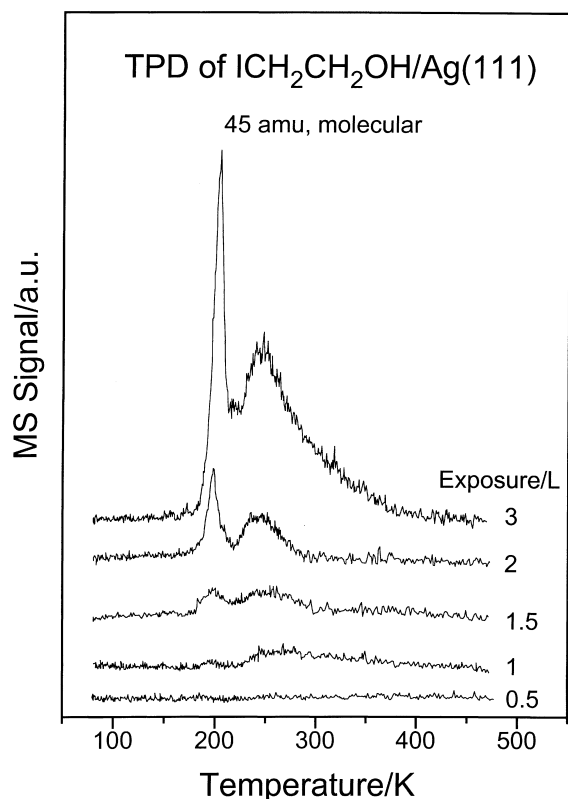
Fig. 4. Iodoethanol (45 amu) temperature-programmed desorption spectra collected as a function of iodoethanol exposure at 80 K. The exposures (in Langmuirs) are marked adjacent to the corresponding spectra.

Table 1
Comparison of the frequencies assigned to a metallacycle on Ag(1 1 0) measured using high-resolution electron energy loss spectroscopy [10] with those formed by adsorbing iodoethanol on Ag(1 1 1) and heating to 240 K measured using infrared spectroscopy[a]

Assignment	Frequency (cm^{-1})	
	Oxametallacycle/ Ag(1 1 0) [10]	Species formed from iodoethanol on Ag(1 1 1) [19]
ν_s(OCC)	793	795
ν_a(OCC)	996	972
ν_a(OCC)	1052	1069
tw(CH_2)	1218	–
w(CH_2)	1273	–
CH_2 sciss	1446	–

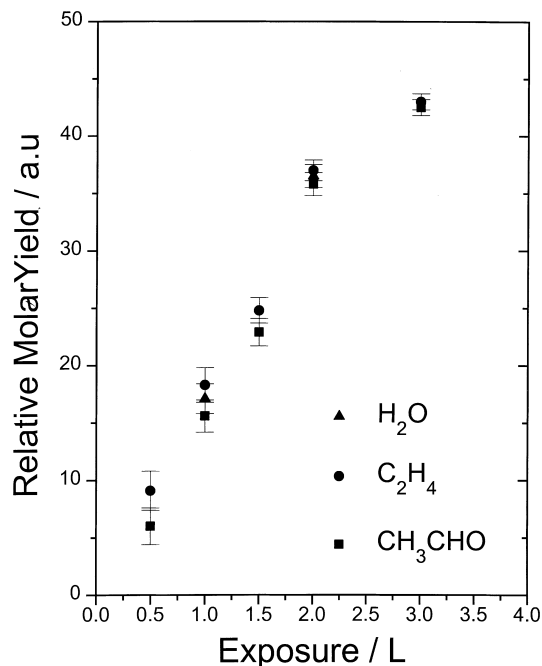[a] sciss: scissor, ν: stretch, tw: twist, w: wag.

Fig. 5. Plot of the relative molar desorption yield of water, ethylene and acetaldehyde in temperature-programmed desorption as a function of iodoethanol exposure.

3.2. Reaction of ethylene and ethylene oxide on oxygen-covered Ag(1 1 1)

Shown in Fig. 6 are the infrared spectra obtained after pressurizing an oxygen-saturated surface with ethylene (1 Torr). The oxygen-covered surface was prepared by an activation process reported in the literature [5–7]. In order to ensure that the spectra are not due to species displaced from the walls of the chamber, control experiments were carried out by pressurizing the cell with 100 Torr of N_2 and collecting RAIR spectra of the oxygen-activated surface. No adsorbate features were detected. The presence of both adsorbed and subsurface oxygen was confirmed using temperature-programmed desorption. Fig. 6(a) shows the spectrum of the surface in the presence of 1 Torr of ethylene. Very intense gas-phase features are detected at ∼2000, ∼1400 and ∼1000 cm^{-1} and are indicated by horizontal lines at the bottom of the spectrum. Additional peaks are detected that are not assignable to gas-phase features and which are due
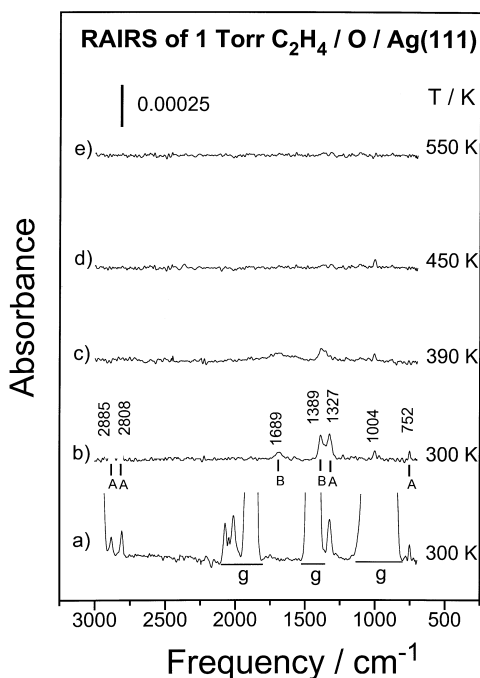
Fig. 6. Reflection-absorption infrared spectra of an oxygen-activated Ag(1 1 1) surface also containing subsurface oxygen pressurized with 1 Torr of ethylene at 300 K. The infrared cell was then evacuated and the spectrum collected at 300 K. The sample was then annealed to various temperatures in ultrahigh vacuum and allowed to cool to 300 K and the infrared spectrum recorded. The annealing temperatures are marked adjacent to the corresponding spectra.

to surface species. These exhibit peaks at 752, 1327, 2808 and 2885 cm^{-1}. These persist when the ethylene is evacuated with the sample held at 300 K (Fig. 6(b)) but with an intensity that is attenuated by about 40%. This indicates that a portion of the species present after pressurizing the surface to ∼1 Torr with ethylene desorb at 300 K. Once the ethylene is removed, additional surface species become evident so that the spectrum collected at 300 K in ultrahigh vacuum exhibits peaks at 752, 1004, 1327, 1389, 1689, 2808 and 2885 cm^{-1}. It is clear that the reaction of ethylene with an oxygen-covered silver surface results in the formation of surface species that are stable at 300 K. None of the features evident in this spectrum can be assigned to adsorbed ethylene which adsorbs weakly on Ag(1 1 1) [20]. In addition, adsorbing ethylene on oxygen-covered Ag(1 1 1) at low exposures (a few

Table 2
Infrared frequencies of the surface species formed by pressurizing an oxygen-activated Ag(1 1 1) surface with ethylene (1 Torr) and evacuating

Frequency (cm^{-1}), C$_2$H$_4$/^{16}O/Ag(1 1 1)	Frequency (cm^{-1}), C$_2$H$_4$/^{18}O/Ag(1 1 1)	$\nu(^{16}O)/\nu(^{18}O)$
752	717	1.049
1004	972	1.033
1327	1303	1.018
1389	1384	1.004
1689	1589	1.063
2808	2810	1.00
2885	2878	1.002

Langmuirs) results in the desorption of ethylene with no reactions occurring at the surface [21]. This is entirely in accord with the work of Grant and Lambert who showed that large ethylene exposures were required to induce a chemical reaction at the surface [5]. It is also interesting to note that ethylene adsorbed at high pressures (several hundred Torr) on clean Ag(1 1 1) at 300 K, desorbs completely reversibly [21]. The majority of the infrared features diminish substantially in temperature as the sample is heated to ∼390 K (Fig. 6(c)) where weak features persist at 1689 and 1389 cm^{-1} and all of the peaks, except for that at 1004 cm^{-1}, are completely removed by annealing to 450 K. These spectral observations are broadly in accord with the temperature-programmed desorption data of Grant and Lambert [5] where an α-state was detected at ∼360 K due to the desorption of acetaldehyde and ethylene oxide, as well as the formation of CO$_2$. The onset of this feature is at 300 K, the starting temperature of the temperature-programmed

Table 3
Ratio of the infrared intensities of modes formed by the adsorption of ethylene oxide and of ethylene adsorption on oxygen-activated Ag(1 1 1)[a]

Frequency(cm^{-1})	I(ethylene oxide)/ I(ethylene)
752 (759)	0.6 ± 0.1
1331 (1330)	0.5 ± 0.1
1389 (1389)	1.4 ± 0.2
1689 (1681)	1.2 ± 0.2
2808 (2808)	0.5 ± 0.1
2885 (2885)	0.4 ± 0.1

[a] Frequencies in parentheses are those measured for ethylene oxide on oxygen-activated Ag(1 1 1).

Table 4
Assignments of the modes assigned to ethylene oxide found following adsorption of ethylene oxide and ethylene on oxygen-activated Ag(1 1 1) (1 Torr at 300 K)

Mode	Ired. Rep	Frequency (cm^{-1})				
		$C_2H_4O_{(g)}$ [26]	C_2H_4O/Ag, UHV 140 K [21]	C_2H_4/O/Ag C_2H_4O/O/Ag, 1 Torr	C_2D_4/^{16}O/Ag, 1 Torr	ν(H)/ν(D) $C_2H(D)_4$/^{16}O/Ag
ν_a(CH(D))$_2$	b$_2$	3065	–	2885	2021	1.42
ν_s(CH(D))$_2$	a$_1$	3006	–	2808	1997	1.41
Ring stretching mode	a$_1$	1271	1265	1331, 1327[a]	999	1.33
Ring deformation mode	a$_1$	877	852	752, 759[a]	–	

[a] Frequencies for ethylene oxide adsorption on oxygen-activated Ag(1 1 1).

Table 5
Assignments of the modes assigned to acetaldehyde found following adsorption of ethylene oxide and ethylene on oxygen-activated Ag(1 1 1) (1 Torr at 300 K)[a]

Mode	Symmetry	Frequency(cm^{-1})			
		Crystalline CH$_3$CHO	CH$_3$CHO/Ag(111), UHV [16]	C_2H_4/^{16}O/Ag C_2H_4O/^{16}O/Ag, 1 Torr	C_2H_4/^{18}O/ Ag, 1 Torr
ν(C=O)	a$'$	1722	1670	1689, 1681[a]	1589
δ_a(CH$_3$)	a$'$	1431, 1422	–	–	–
δ(CH)	a$'$	1389	–	–	–
δ_s(CH$_3$)	a$'$	1347	1400	1389, 1389[a]	1384
ν_a(OCO)	a$'$	–	–	–	–
ν_s(OCO)	a$'$	–	1034	–	–
ν(C–C)	a$'$	1118	–	–	–

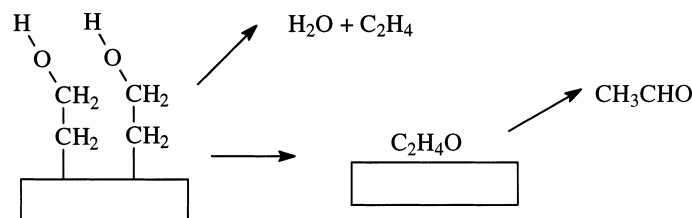[a] Frequencies for ethylene oxide adsorption on oxide-activated Ag(1 1 1), δ: deformation.

desorption spectrum. The diminution in intensity of the infrared features in the presence of 1 Torr of ethylene (Fig. 6(a)) and after evacuation (Fig. 6(b)) suggests that the desorption state, in fact, extends below 300 K and the feature detected at ∼360 K represents the trailing-edge portion of the whole desorption state. Similar experiments were carried out by pressurizing an oxygen-activated surface prepared using ^{18}O with ethylene (C$_2$H$_4$). The resulting frequencies are summarized in Table 2. Experiments were also carried out by pressurizing a ^{16}O-activated surface with C$_2$D$_4$ and ethylene oxide and these results are presented in Tables 3, 4 and 5.

4. Discussion

Iodoethanol adsorbs at 80 K on Ag(1 1 1) to form a condensed layer that desorbs at ∼205 K (Fig. 1,

Table 1). The infrared spectra observed following initial adsorption are consistent with the removal of iodine from iodoethanol to form a hydroxy ethyl species [19]. Subsequent reaction of this species yields equimolar amounts of ethylene and water in a simultaneous reaction and is illustrated in Scheme 1 below.

This reaction also deposits species of molecular formula C$_2$H$_4$O on the surface which subsequently desorb as acetaldehyde at 260 and 315 K (Figs. 1 and 2). The equimolar amount of acetaldehyde produced as ethylene and water is in accord with this scheme (Fig. 5). Broadly similar reaction products are found on Ag(1 1 0) except that ethylene, water and acetaldehyde all desorb simultaneously [9] so that subsequent reaction of the species of stoichiometry C$_2$H$_4$O appears to be rather rapid on Ag(1 1 0). Almost equimolar amounts of water and ethylene desorb from Ag(1 1 0). However, the amount of acetaldehyde

$$H_2O + C_2H_4$$

$$\begin{array}{cc} H & H \\ | & | \\ O & O \\ \diagdown & \diagdown \\ CH_2 & CH_2 \\ | & | \\ CH_2 & CH_2 \end{array} \qquad C_2H_4O \qquad CH_3CHO$$

Scheme 1.

is approximately twice that predicted by Scheme 1. This implies that there may be an additional dehydrogenation pathway available on Ag(1 1 0) not seen on Ag(1 1 1).

The nature of the species of stoichiometry C_2H_4O formed on the surface as a result of the reaction depicted in Scheme 1 have been identified using reflection-absorption infrared spectroscopy [19]. In particular, a species exhibiting infrared frequencies at 795, 972 and $1069\,cm^{-1}$ is assigned to an oxametallacycle and compared to the frequencies of an oxametallacycle on Ag(1 1 0) [10] in Table 1, where the higher frequency CH_2 modes are not detected since they are relatively weak. The agreement between the two sets of data are reasonably good. The major discrepancy is that the $996\,cm^{-1}$ peak is the most intense in the electron energy loss data for Ag(11 0) [10] while the $1069\,cm^{-1}$ peak is the most intense in the infrared spectra for Ag(1 1 1). There may be two possible causes for these intensity differences. First, the HREELS data may also contain contributions from impact scattering and second, the oxametallocycle structure on Ag(1 1 1) may be different to that on Ag(1 1 0). This species thermally decomposes at 260 K to yield acetaldehyde suggesting that an oxametallacycle, if it forms on Ag(1 1 1) from a reaction of ethylene and adsorbed atomic oxygen, does not lead to ethylene oxide formation.

The work of Grant and Lambert on the chemistry of ethylene on oxygen-covered Ag(1 1 1) suggests that the presence of both adsorbed and subsurface oxygen are required for the formation of ethylene oxide [5]. Adsorbed atomic oxygen is responsible for both total oxidation to form CO_2 and water as well as ethylene oxide. Two total oxidation pathways were identified. The first was a direct combustion of adsorbed ethylene that does not require the presence of subsurface oxygen and produced an α-CO_2 desorption state at ~360 K. The second pathway involves the further oxidation of ethylene oxide and requires the presence of subsurface oxygen and appears to proceed via CH_3CHO, CH_3COOH and $(COOH)_2$ and gives rise to a β-CO_2 desorption state at ~450 K. The kinetic deuterium isotope effects indicate that C–H bond scission is rate-determining in both total oxidation pathways [11,12]. The infrared measurements are in broad agreement with these observations since the majority of the infrared features disappear at ~390 K corresponding to ethylene oxide/acetaldehyde desorption and the α-CO_2 state and a feature at ~$1004\,cm^{-1}$ persists at this temperature but disappears on heating to above 450 K corresponding to the β-CO_2 desorption state (Fig. 6).

Ethylene adsorbs only weakly and reversibly on clean Ag(1 1 1) and is only slightly perturbed by the presence of co-adsorbed oxygen when exposed at a sample temperature of 80 K [21]. Ethylene adsorbed on Ag(1 1 1) exhibits a sharp feature at $950\,cm^{-1}$ which shifts to ~$970\,cm^{-1}$ in the presence of adsorbed oxygen [21]. No features are detected at these frequencies after pressurizing the surface (Fig. 6) indicating that no ethylene appears to be bonded directly to the silver surface under these circumstances, but that all products are formed by reaction with adsorbed atomic oxygen. This reaction also appears to be activated. Similar species also appear to be formed following the adsorption of both ethylene and ethylene oxide on oxygen-covered silver (Table 4).

It was found that the frequencies of features formed by pressurizing oxygen-activated Ag(1 1 1) with ethylene or ethylene oxide were identical. Their relative intensities were, however, different and their relative

intensities are displayed in Table 3. This allows the modes to be classified into two groups, one with frequencies at 752, 1327, 2808 and 2885 cm^{-1} (designated species A in Fig. 6) the other with frequencies at 1389 and 1681 cm^{-1} (designated species B in Fig. 6). The 1330 and 752 cm^{-1} modes involve the participation of oxygen (Table 2) while the 2808 and 2885 cm^{-1} modes are due to C–H stretches (Table 4). The frequencies of species A are consistent with the presence of an epoxide ring and the assignments are shown in Table 4. The 752 cm^{-1} peak is assigned to a ring deformation mode (a_1 symmetry) and is shifted by $\sim$125 cm^{-1} from the corresponding gas-phase value. This shift is larger than that for ethylene oxide chemisorbed on oxygen-covered Ag(1 1 1) at 160 K where the shift is $\sim$25 cm^{-1} [21]. This implies that the epoxide ring is substantially distorted when formed at 300 K at high pressures. The peak at 1330 cm^{-1} is assigned to a ring stretching mode (a_1 symmetry) which appears at 1271 cm^{-1} in the gas-phase and is thus, shifted by $\sim$60 cm^{-1}. The observed isotopic shifts found with ^{18}O (Table 2) and D (Table 4) substitution are consistent with this assignment. The peaks at 2885 (b_2 symmetry) and 2808 cm^{-1} (a_1, symmetry) are assigned to C–H stretching modes. Again the isotopic shifts are consistent with this assignment and the shifts compared to the gas-phase values (180 and 198 cm^{-1}, respectively) are also consistent with considerably rehybridized carbons in the epoxide ring. The appearance of an intense C–H stretching mode with b_2 symmetry (at 2885 cm^{-1}) suggests that the epoxide is not oriented with the principle symmetry axis of the adsorbed ethylene oxide perpendicular to the surface since this would result in the appearance of modes with just a_1 symmetry [22]. Note that the adsorption of ethylene oxide on Ag(1 1 1) at low pressures displays only modes with a_1 symmetry implying perpendicular adsorption in that case [21]. Modes of b_2 symmetry transform as a vector oriented along the x direction (perpendicular to the epoxide ring). The appearance of modes with this symmetry suggests that the epoxide ring is oriented in such a way that a component of this vector is normal to the surface. There is no evidence for the appearance of modes with b_1 symmetry implying that the C–C bond of the epoxide ring remains oriented parallel to the surface. This suggest a molecular orientation as depicted below.
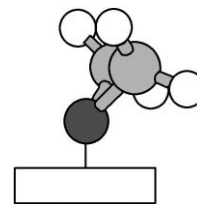
The remaining features (at 1389 and 1681 cm^{-1}; Table 3) due to species B (Fig. 6) are assigned to the presence of adsorbed acetaldehyde and the assignments are summarized in Table 5. The 1689 cm^{-1} feature is assigned to the C=O stretching mode and the isotopic shift with ^{18}O is consistent with this assignment and this frequency is relatively close to that found for acetaldehyde adsorbed in ultrahigh vacuum on Pd(1 1 1) [23], Ru(0 0 1) [24] and Cu(1 1 1) [25]. Note that these modes are also the most intense for the infrared spectrum of acetaldehyde adsorbed on Ag(1 1 1) at 80 K [16].

5. Conclusions

2-Iodoethanol adsorbs on Ag(1 1 1) at 80 K and is proposed to react at relatively low temperatures to form 2-hydroxyethyl species and deposit iodine onto the surface. These react to eliminate water and simultaneously desorb ethylene to leave a surface fragment of stoichiometry C_2H_4O. Surface infrared data suggest that an oxametallacycle is formed which thermally decomposes at $\sim$260 K to desorb acetaldehyde. Both ethylene oxide and ethylene adsorb and react on oxygen-activated Ag(1 1 1) at high pressures to form adsorbed acetaldehyde and ethylene oxide. Adsorbed ethylene oxide is substantially distorted from its gas-phase geometry as judged by the shifts in its vibrational frequencies and appears to be adsorbed via the oxygen atom to the surface with its molecular plane tilted to the (1 1 1) plane. The adsorbed ethylene oxide coverage is larger when the surface is pressurized by 1 Torr of ethylene at 300 K than when the surface is subsequently evacuated suggesting that a portion of the ethylene oxide desorbs even at 300 K. All of the adsorbed ethylene oxide is removed by annealing in vacuo to 390 K while a portion of the adsorbed acetaldehyde persists at this temperature.

This is completely removed on heating to 450 K. These observations are consistent with previous temperature-programmed desorption data for ethylene and ethylene oxide on oxygen-covered Ag(1 1 1).

Acknowledgements

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