Catalysis Letters 26 (1994) 109–121

Oxidation of Cl-modified Ag(111) under UHV conditions and ethylene adsorption on the oxidized surface

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Received 10 November 1993; accepted 3 March 1994

Oxidation of Cl-modified Ag(111) under UHV conditions was investigated using AES, ISS and HREELS. The results showed that Cl-modified Ag(111) can be easily oxidized at 550 K by 1×10^{-6} mbar oxygen which was also heated to 550 K. With HREELS two fundamental vibrations at 600 and 1000 cm^{-1} were detected for silver oxide and the multiple losses and combination excitations as well. Ethylene adsorption on the oxide was analyzed by HREELS. Surface hydroxyl species was formed at 230 K and stable to above 300 K, which is attributed to silver oxide. Ethylidyne was suggested to form concurrently with hydroxyl species.

Keywords: Cl-modified Ag(111); oxidation; phonons; ethylene adsorption

1. Introduction

Interest in silver catalyst stems from its unique catalytic properties in two industrial processes: ethylene epoxidation and methanol selective oxidation to formaldehyde [1,2]. Studies also focused on the promoter action of chlorine [1]. Most of the research in the past was carried out on silver single crystals with surface science techniques. Though much progress has been made recently [3–8] in understanding the fundamental questions of the partial oxidation processes, some fundamental aspects are still equivocal. Madix's and Lambert's groups [3–8] have shown with conceivable evidence that the active oxygen species involved in epoxidation and some partial oxidation processes on silver is atomic oxygen, which is against the dioxygen hypothesis first brought by Worbs [9] and further developed by Kilty and coworkers [10,11]. Meanwhile, Van den Hoek et al. [12] suggested that subsurface oxygen plays some role in ethylene epoxidation through their theoretical calculations. However, little work has been done on the effect of subsurface oxygen up to now. Rehren et al. [13] even suggested from their TPD results that on a polycrystalline Ag the so-called dissolved or subsurface oxygen which desorbs at 725 K or higher in previous reports [14,15] is actually chemisorbed atomic oxygen, while the oxygen species desorbing at 595 ± 25 K was identified as the dissolved oxygen. The same authors found that oxygen is dissolved in silver even at 300 K.

For the promoter action of chlorine, Campbell et al. [16–18] have done a series of research and showed that chlorine acts through an ensemble effect. Lambert et al. [6,19] suggested that chlorine promotes through an electronic effect, that is, chlorine modifies the properties of atomic oxygen through Ag atoms. Van Santen et al. [1] proposed that chlorine has an effect similar to that of subsurface oxygen, thus the effect of chlorine is also electronic.

Our previous studies [20–22] on adsorption of chlorine and oxygen on Ag(111) showed that chlorine adsorption to a high exposure can induce the formation of defects, which was evidenced by the following experimental results: (i) the LEED pattern showed a high background; (ii) a wide vibrational feature centered at about 800 cm^{-1} was detected by HREELS, and (iii) the work function of the Cl-modified Ag(111), which means the Ag(111) was exposed to chlorine at a high exposure and then heated to about 673 K to remove chlorine but without any annealing at a higher temperature, decreased by 0.3 eV compared with that of a clean Ag(111). Through the study of the effect of chlorine adsorption on oxygen adsorption, we found that chlorine acts through a structural effect rather than an electronic effect [21,22]. Although the nature of the defects induced by chlorine adsorption is unknown, it is substantiated that the defects can accelerate the diffusion of surface atomic oxygen into the bulk to become subsurface oxygen where we followed the definition of subsurface oxygen of most of the previous studies. From these results, we expected that the defects induced by chlorine adsorption might play a certain role in ethylene epoxidation.

In this letter, we report the oxidation of Cl-modified Ag(111) under UHV conditions. We surprisingly found by means of AES and HREELS that Cl-modified Ag(111) can be readily oxidized under UHV conditions in contrast with previous findings by other investigators that silver single crystals can only be oxidized under a much higher pressure, i.e. several Torrs or higher. After preparing the oxidized Ag(111), we extend our study on ethylene adsorption on this sample.

2. Experimental

Experiments were performed in an UHV system from Leybold with LEED, ISS, UPS, AES, HREELS (ELS-22) and mass spectroscopy (Q200). The base pressure was 3×10^{-10} mbar. HREELS spectra were tuned for 72–96 cm^{-1} resolution (FWHM) with an incident electron beam energy of 4.0 eV. The resolution was broadened by the defects produced by chlorine adsorption and was generally about 56–72 cm^{-1} if a repolished and well-defined Ag(111) sample was used. All the HREELS spectra were recorded in the specular mode. Helium was employed as the ISS probe beam. The ion gun for ISS has a Brink-type ionizer with the ion beam, focused by a two-cylinder electronic optics, striking the surface at 45°. The scattering angle was 135°. The primary energy of the ion beam was 1000 eV, similar results were obtained with 500 eV. The ion current was in the order of 0.1–1 μA. The noise level was adjusted to 10 cps. In this study, the Ag signal was (1–5) $\times 10^4$ cps and the enlarged O signal, (1– 2.5) $\times$ 10^2 cps approximately. For non-differentiated Auger electron spectroscopy, the signal intensities were (1–5)$\times 10^5$ cps with a primary electron beam energy of 1000 eV, a peak-to-peak voltage of 5 V and a transmission energy of 20 eV. A 3000 eV electron beam was used for differentiated AES experiments.

The Ag(111) sample was prepared by mechanical polishing and etched in a dilute $NH_3 \cdot H_2O$ solution. The crystal surface was cleaned by 1500 eV Ar^+ ion bombardment and annealed to 825 K. Surface cleanliness and structure were monitored by AES, HREELS and LEED. Sample temperature was measured with a Pt–Pt/Rh thermocouple welded to the back of the sample. Cl vapor was generated by electrolysis of pelletized AgCl in an electrochemical cell as described before [20,21]. Chlorine adsorption was carried out at room temperature, ca. 300 K. In this experiment, the amount of chlorine was 30 min times the constant electrolysis current of 5 μA, corresponding to about 20 L or a little higher. After this chlorine adsorption, the Ag(111) sample was heated to 673 K to remove chlorine but without annealing to higher temperatures in order that the defects produced by chlorine adsorption were kept, the sample through these treatments was called Cl-modified Ag(111).

Research grade oxygen and ethylene were used for oxidation or adsorption and were checked by means of an in situ mass spectrometer. The exposure of ethylene was reported in langmuir units calculated from an uncorrected ion gauge reading. In order to activate oxygen for oxidation, a special effusive tube was designed. It consists of a Φ35 flange. A Kovar and four conducting wires for resistive heating and temperature measurement by a chromel–alumel thermocouple seated on the flange. The stainless steel side of the Kovar was welded and connected to the hole on the flange and the quartz side was thermally lengthened to make the wall of the quartz tube thinner to guarantee effective thermal conductivity as possible as it can. A tantalum resistive wire wraps the other side of the quartz wall densely and the thermocouple was sintered in the wall near the mouth of the quartz tube. In this designation, the oxygen molecules in molecular flow region only strike the inner wall of the quartz tube and if the quartz tube is heated to hundreds of kelvins, one oxygen molecule can strike the wall for at least three times before it leaves so that the oxygen molecules can obtain the thermal energy and are estimated to be with a temperature near to that of the wall in our experimental temperature region. The effusive mouth of the quartz tube was about Φ3 in diameter and was 5–10 mm away from the surface of the sample. In oxidation, the input oxygen molecules were heated to about 550 K and the sample was also kept at 550 K.

3. Results

3.1. OXIDATION OF Cl-MODIFIED Ag(111)

Before we go on, we first clarify the meanings of different samples. "Clean Ag(111)" means the Ag(111) sample which, without a history of chlorine adsorption, was cleaned and annealed at 823 K until a LEED pattern (1 × 1) was shown. "Cl-modified Ag(111)" means the "clean Ag(111)" sample which was exposed to chlorine at a high exposure as indicated in the Experimental section and subsequently heated to 673 K to remove chlorine but without any annealing at a higher temperature. "Oxidized Ag(111)" means the "Cl-modified Ag(111)" sample which was oxidized at 550 K by 550 K oxygen of 1×10^{-6} mbar.

Fig. 1 shows the AES spectra of Cl-modified Ag(111) oxidized by 550 K oxygen of 1×10^{-6} mbar oxygen for different times. Fig. 1a is for cleanly Cl-modified Ag(111). The absence of the 182 eV peak for the Cl LMM Auger transition indicates the chlorine has been removed completely in our AES detection limit. Compared with the standard AES of Ag, no contamination was found by AES, and also by HREELS. The carbon signal usually mixes with the Ag Auger transition at about 260 eV so that it is difficult to judge whether carbon contamination exists. In this work, we use the intensity ratio of the Ag transition at 260 eV to that at 300 eV to monitor carbon contamination extent. If the intensity ratio falls below

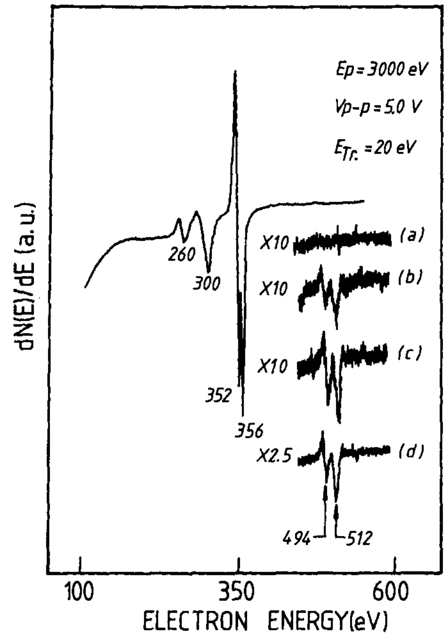

Fig. 1. AES of Cl-modified Ag(111) oxidized by 550 K oxygen of 1×10^{-6} mbar at 550 K for different times. (a) 0 h, (b) 1.0 h, (c) 4.5 h, and (d) >10 h.

the value of about 0.47 which is derived from standard Ag AES spectrum, we hold that the surface is free of carbon. After oxidation of the Cl-modified Ag(111) at 550 K for 1 h by 1 × 10^{-6} mbar oxygen which was also heated to 550 K through the effusive tube, two small peaks at 494 and 512 eV (fig. 1b) characteristic of O KLL Auger transitions showed that there exists oxygen on the sample. With continuing oxidation (figs. 1c and 1d), the two oxygen peaks increase gradually.

The non-differentiated Auger electron spectrum for Al-modified Ag(111) after oxidation for 4.5 h by 550 K oxygen of 1 × 10^{-6} mbar at 550 K, is given in fig. 2b. Five peaks at 345.6, 349.2, 350.8, 354.3 and 355.8 eV appear. Fig. 2a displays the AES spectrum for clean Ag(111) under the same treatment conditions. Two peaks at 350.8 and 355.8 eV are seen in fig. 2a. These two peaks are typical Auger transitions of Ag MNN. Thus, comparing figs. 2a and 2b, one can find that after oxidation by 550 K oxygen, three additional peaks at 345.6, 349.2 and 354.3 eV appear for Cl-modified Ag(111).

Fig. 3 gives the corresponding HREELS spectra for Cl-modified Ag(111) oxidized by 550 K oxygen of 1 × 10^{-6} mbar for different times. After oxidation for 1 h, four vibrational features at 600, 896, 1204 and 1480 cm^{-1} appear in fig. 3a where the 600 cm^{-1} feature is dominant. After oxidation for 4.5 h, five peaks at 600, 1000, 1584, 2000 and 2984 cm^{-1} appear in fig. 3b where the peak at 1000 cm^{-1} becomes dominant. With further oxidation for > 10 h (fig. 3c), the same peaks as in fig. 3b are seen, but the peak at 1000 cm^{-1} is stronger and so are the three peaks at 1584, 2000 and 2984 cm^{-1}. Heating the sample to 680 K, we obtain the spectrum in fig. 3d. In fig. 3d, all the peaks become weaker. If we view the peak at 896 cm^{-1} in fig. 3a and the peak at 1000 cm^{-1} in figs. 3b–3d as from the same vibrational

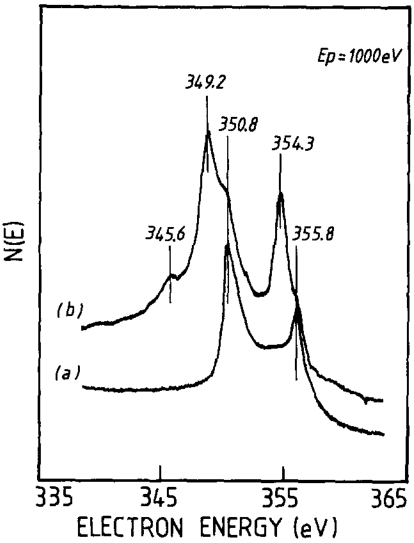

Fig. 2. Non-differentiated AES for (a) clean Ag(111) oxidized by 550 K oxygen of 1 × 10^{-6} mbar at 550 K for 4.5 h and for (b) Cl-modified Ag(111) oxidized under the same conditions.

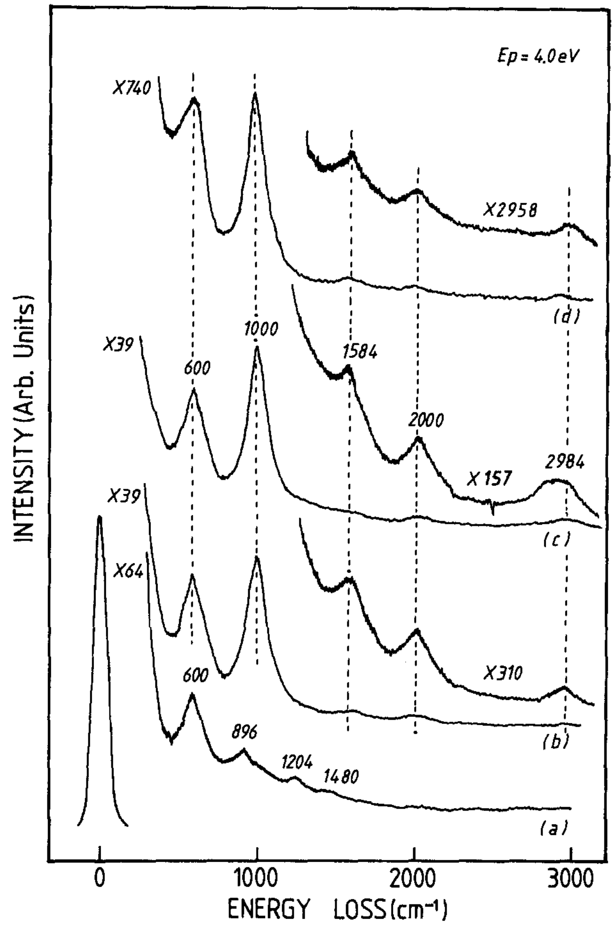

Fig. 3. HREELS for Cl-modified Ag(111) oxidized by 550 K oxygen of 1×10^{-6} mbar at 550 K for various times. The spectra were recorded at room temperature. (a) 1.0 h, (b) 4.5 h, (c) >10 h, and (d) heated to 680 K.

source but only differing in frequency, we now define *the intensity ratios* R_1*,* R_2 *and* R_3 *as the peak intensities of 1000 or 896* cm^{-1}*, 1584 or 1480* cm^{-1} *and about 2984* cm^{-1} *to that of 600* cm^{-1} *respectively.* These R values are listed in table 1. Obviously, the R values, especially R_1, relate to the oxidation extent. The aim of the definition of the intensity ratio is that in the later text describing ethylene adsorption, we can use the variations of R values to judge the existence of adspecies because their vibrational features overlap unfortunately with those in fig. 3.

Fig. 4b shows the ISS spectrum for Cl-modified Ag(111) oxidized by 550 K oxygen of 1×10^{-6} mbar at 550 K. Fig. 4a is the ISS spectrum for clean Ag(111) oxidized under the same conditions. The signal at E/E_0 near 0.4 is characteristic of oxygen. Therefore, the two spectra demonstrate that oxidized by 550 K oxygen of 1×10^{-6} mbar, there are oxygen atoms in the topmost layer of Cl-modified Ag(111), while there are no oxygen atoms in that of clean Ag(111).

Table 1
Values of intensity ratios from fig. 3[a]

Figure	$R_1(10^{-1})$	$R_2(10^{-2})$	$R_3(10^{-2})$
3a	3.0	4.0	–
3b	15.4	5.2	2.9
3c	20.0	9.5	7.0

[a] See the text for the definition of each intensity ratio. The experimental error for every value is ±0.5.

3.2. ETHYLENE ADSORPTION ON OXIDIZED Ag(111)

Ethylene can chemisorb on Ag only if oxygen preadsorbs. We have shown with ISS that on oxidized Ag(111), there is oxygen in the topmost layer. So it is expected that ethylene can adsorb on the oxidized Ag(111) surface. This is shown in fig. 5. All the HREELS spectra in fig. 5 were recorded at about 140 K after the sample was heated to the indicated temperature. Fig. 5a is the background spectrum of oxidized Ag(111) with the value of R_1 being 2.0. The small peaks at 1550 and 2010 cm^{-1} are also available. Fig. 5b is the HREELS spectrum for ethylene at 140 K in which the value of R_1 is 4.4. In addition, three relatively stronger features at 1320, 1584 and 2984 cm^{-1} are seen with reference to those in the background spectrum. The new feature at 1320 cm^{-1} is indicative of adsorbate(s) on the surface.

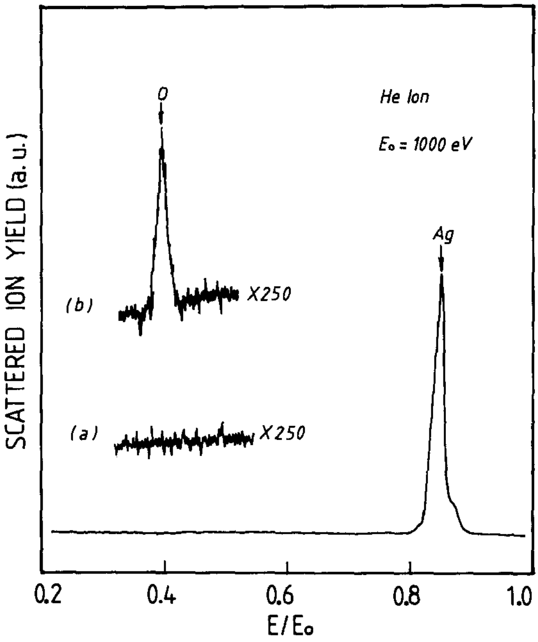

Fig. 4. ISS of different samples oxidized by 550 K oxygen of 1 × 10^{-6} mbar at 550 K for 1 h. (a) Clean Ag(111) and (b) Cl-modified Ag(111).

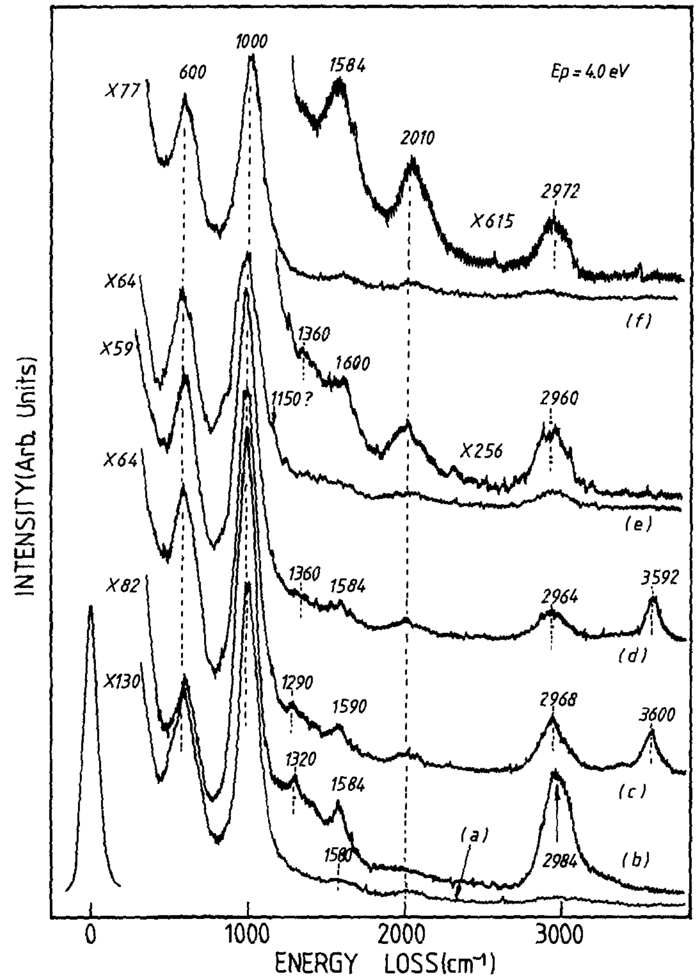

Fig. 5. HREELS of 30 L ethylene on oxidized Ag(111) which was prepared by oxidation of Cl-modified Ag(111) at 550 K oxygen of 1×10^{-6} mbar for >10 h. All the spectra were collected at 140 K after heating the sample to the indicated temperature. (a) 0 L ethylene and (b) 30 L ethylene at 140 K, and heated to (c) 230 K, (d) 300 K, (e) 400 K, and (f) 550 K.

The strong peak at 2984 cm^{-1} shows that the adspecies comprises a CH group. The R_1 value, 4.4, suggests that there is a peak over the original one at 1000 cm^{-1}. Similarly, a peak at 1590 cm^{-1} can also be isolated from the change of R_2 value (table 2). Therefore, after adsorption of ethylene at 140 K, we get four vibrational features at 1000, 1320, 1590 and 2984 cm^{-1}. Upon warming the sample to 230 K, we obtain fig. 5c in which a further new peak at 3600 cm^{-1} grows. This peak exists till 400 K (see, figs. 5d and 5e). The HREELS spectrum after heating to 550 K is depicted in fig. 5f. We list the values of R_1, R_2 and R_3 in table 2 for convenience of further analyses.

Table 2
Values of intensity ratios from fig. 5 [a]

Figure	$R_1(10^{-1})$	$R_2(10^{-2})$	$R_3(10^{-2})$
5a	20.0	9.5	7.0
5b	44.0	47.1	125.7
5c	24.5	14.2	40.8
5d	21.3	11.5	19.2
5e	19.7	9.6	13.8
5f	19.5	10.0	6.9

[a] The definitions and experimental error are the same as in table 1.

4. Discussion

We begin our discussion with the oxidation of Cl-modified Ag(111). Two Auger transitions at 349.2 and 354.3 eV in fig. 2 demonstrate clearly the valence state change of Ag. Sesselmann and Chuang [23] and Bowker and coworkers [24,25] in their research on Ag metals exposed to chlorine by XAES showed a similar Ag electron energy down-shift of about 2.0 eV and attributed it to the formation of AgCl, which was also supported by our study on the Cl/Ag(111) system [20]. Moreover, on a pure Ag_2O solid [26], two Auger transitions of Ag $M_{4,5}NN$ at the similar energy positions as in fig. 2b have been reported. All these lead to the conclusion that Ag_2O was formed on Cl-modified Ag(111) provided it is oxidized at 550 K by 550 K oxygen of 1×10^{-6} mbar. This conclusion finds further evidence from HREELS results described below. The mysterious Auger transition at 345.6 eV is not understood presently.

Fig. 3 shows two strong peaks at 600 and 1000 cm^{-1} (or 896 cm^{-1}) in every spectrum. The intensities vary in accordance with the oxidation extent of the sample. They apparently cannot be viewed as the vibrations of surface atomic oxygen and/or dioxygen which had been reported with frequencies of 300–340 cm^{-1} for ν_{Ag-O} and 600–640 cm^{-1} for ν_{O-O} respectively [21,27,28]. Additionally, the vibrational intensities of surface atomic oxygen and dioxygen cannot be so strong as those below 1000 cm^{-1} in fig. 3. Accordingly, the peaks at 600 and 1000 cm^{-1} (or 896 cm^{-1}) should be excluded from the vibrations characteristic of surface atomic oxygen and dioxygen. Actually, oxides usually give HREELS spectra with the characters as in fig. 3. For instance, for Al_2O_3, Venus et al. [29] detected three fundamental vibrations at 420, 625 and 845 cm^{-1} while Chen et al. [30] detected similar vibrations at 430, 650 and 870 cm^{-1}. For $TiO_2(100)$, Kesmodel and coauthors [31] found two fundamental features at 436 and 766 cm^{-1}. In these studies, some double or triple losses and the combination excitations of the strong fundamentals were also seen. Following these reports, we can assign the features at 600 and 1000 cm^{-1} (or 896 cm^{-1}) as the fundamentals of silver oxide. Therefore, the peaks at 1204 and 1480 cm^{-1} in fig. 3a are attributed to the double loss of the 600 cm^{-1}

feature and the combination excitation of the 600 and 896 cm^{-1} losses. Similarly, the 1584 cm^{-1} feature in figs. 3b–3d is due to the combination of 600 and 1000 cm^{-1} losses and the 2000 and 2984 cm^{-1} features due to the double and triple losses of the 1000 cm^{-1} feature respectively. In fig. 3, the following phenomena are noted: (i) the frequency of the 896 cm^{-1} feature in fig. 3a shifts up to 1000 cm^{-1} in figs. 3b–3d; (ii) the double loss at 1204 cm^{-1} of the 600 cm^{-1} feature in fig. 3a disappears or obscures in figs. 3b–3d while in the latter figures appears the double loss at 2000 cm^{-1} of the 1000 cm^{-1} feature; (iii) during oxidation, the intensity of the fundamental at 1000 cm^{-1} becomes stronger and stronger and so do the combination excitation and the multiple losses, which can be seen in table 1; (iv) the triple loss of the 1000 cm^{-1} feature is observed in figs. 3b–3d; and (v) after being heated to 680 K, all the peaks become much weaker (cf. fig. 3d and figs. 3a–3c). The frequency shift from 896 cm^{-1} to 1000 cm^{-1} might be due to dipole interaction or to the structure change during the oxidation or it might be due to a different excitation. The real reason is yet unknown. To our knowledge, there are no reports with the similar experimental observation. Anyhow, the formation of silver oxide on Cl-modified Ag(111) after oxidation at 550 K by 550 K oxygen under UHV conditions can be judged from figs. 2 and 3.

Heated to 680 K, the produced silver oxide (fig. 3d) did not decompose completely or reduced though silver oxide generally decomposes below 620 K [32]. That all the R values in fig. 3d are almost the same as those in fig. 3c demonstrates that the weakening of all the losses cannot be solely due to the decomposition of silver oxide nor due to the desorption of silver oxide, which desorbs at a much higher temperature. Thus, it suggests that upon heating, underlying or neighbouring silver atoms may come up to block the oxide so that the losses cannot be completely detected by HREELS. Ag is the smaller entity and its diffusivity should be higher than that of silver oxide.

Generally, silver single crystals are oxidized at a much higher pressure. Under our UHV conditions, we did not find any evidence for the formation of silver oxide if clean Ag(111) is oxidized by 550 K oxygen or Cl-modified Ag(111) oxidized by 300 K oxygen. This implies that oxidation of Cl-modified Ag(111) under UHV conditions needs two necessary factors: the defects induced by Cl adsorption [20] and the activation of oxygen. The former suggests that silver oxide may be formed through nucleation as the defects can be employed as nuclei centers and the latter hints that there exists an activation energy barrier in the formation of silver oxide.

From figs. 1b and 4b, we calculated that the signal intensity of oxygen in AES was about tens of times of that in ISS under the same oxidation conditions. It seems to tell that silver oxide is formed in three dimensions rather than in two dimensions. If so, silver oxide must grow along the defect channel into the bulk, as we had assumed in a previous paper [20] that the defects were initially produced on the boundary of AgCl and Ag crystallites and the defects act as the penetration channels for the diffusion of surface Cl atoms [20] and oxygen atoms [21] into the subsurface or bulk.

Due to the existence of oxygen atoms in the topmost layer, ethylene is expected to adsorb on oxided Ag(111). Fig. 5b shows that at 140 K ethylene is molecularly adsorbed on or weakly π-bonded to the oxide surface. Vibrational features at 1000, 1320, 1584 and 2985 cm^{-1} appear clearly though they unfortunately overlap with the optical phonon peaks of silver oxide at the same energy positions. This can be seen in table 2. After Nyberg et al. [33] and Backx et al. [28] and Stuve and Madix [34], the four peaks can be easily assigned as: 1000 cm^{-1}, CH_2 out-of-plane bend; 1320 cm^{-1}, CH_2 scissor; 1584 cm^{-1}, C=C stretch; and 2984 cm^{-1}, CH stretch. Upon warming to 230 K (fig. 5c) and 300 K (fig. 5d), a new feature at 3600 (3592) cm^{-1} appears. From table 2, it is quite certain that ethylene exists most probably in a mixture with other adspecies. Ethylene on silver desorbs below 200 K [28]. Thus, the existence of ethylene up to 300 K seems strange. A possible explanation is that silver oxide can stabilize ethylene through the electron-deficient $Ag^{\delta+}$ ion sites as the electron acceptor for the π-electrons in ethylene. The peak at 3600 (3592) cm^{-1} should be from surface hydroxyl species [35–37]. Again, this is in contradiction with previous results that hydroxyl species on metals including Ag cannot be stable at 300 K or above. Thus, it is also assumed that silver oxide is responsible for the existence of hydroxyl species at room temperature. We note that Peden and Houston [38] have reported that hydroxyl species can be stable even up to 600 K on an oxidized Rh surface.

At 400 K, the R_1 and R_2 values (table 2) in fig. 5e decreased back to those in fig. 5a. This suggests that the two characteristic vibrations for CH_2 out-of-plane bend and C=C stretch of ethylene vanished and hence, there was no ethylene on the surface at 400 K. However, the R_3 value, relating to the intensity of 2960 cm^{-1}, in fig. 5e was almost twice that in fig. 5a. Another peak which can be seen clearly centers at 1360 cm^{-1}. These two features show that there still exists adspecies comprising CH group(s) on the surface. A shoulder at about 1150 cm^{-1} on the right side of the 1000 cm^{-1} peak in fig. 5e seems present but is somewhat dim due to the strong feature of 1000 cm^{-1}. If the existence of the shoulder feature is granted, then we have three vibrations for the adspecies on the surface at 400 K. These features are analogous to those for adsorbed ethylidyne [39–41]. At 400 K, hydroxyl species disappeared, suggesting that it disproportionates or reacts with hydrogen atoms in other species into water which desorbs quickly.

Now, we go back to ethylene adsorption on the surface at 230 and 300 K. If the identification of ethylidyne at 400 K is correct, it indicates that there is possibly ethylidyne at 230 and 300 K on the surface too. That implies that adsorbed ethylene may react with oxygen atoms in the oxide to give ethylidyne and hydroxyl species. At 550 K, ethylidyne vanished (fig. 5f). Our data do not permit to analyze in detail how and by which path ethylidyne decomposes or reacts with oxygen atoms in the oxide. Finally, we should point out that some relating vibrational features were not detected. For hydroxyl species, a relatively intense peak at about 750 cm^{-1} for the δ_{OH} mode is expected; for adsorbed ethylene and ethylidyne, a peak near 300–500 cm^{-1} for the stretch of adspecies against the surface is also expected. However, we failed to detect these two features in fig. 5. The most possible reason is that the phonon peaks of silver oxide are too strong to observe other smaller peaks, especially in the region of 450–750 cm^{-1} and 850–1150 cm^{-1}.

5. Conclusion

Our experimental results showed that Cl-modified Ag(111) can be readily oxidized at 550 K by 550 K oxygen under UHV conditions. The easy oxidation of the surface is attributed to the defects induced by chlorine adsorption. Silver oxide can stabilize hydroxyl species and ethylene.

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