Formation of channels for oxygen migration towards subsurface sites by CO oxidation and growth of the surface oxide phase on Ag(001)

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Abstract

The mechanism of oxygen incorporation in Ag is still poorly known. As recently demonstrated [Phys. Rev. B 63 (2001) R1404], oxygen adatoms removal by CO oxidation leaves the Ag(001) surface in a modified state in which oxygen segregation from the bulk and the formation of a surface oxide phase can be induced by further CO exposure. Here we show that the same channels, forming during CO oxidation and linking surface and subsurface sites, allow also for the migration of oxygen adatoms into the subsurface region. When dosing O2 on an Ag(100) surface, on which oxygen had been previously removed by CO oxidation, we observe indeed the formation of the same surface oxide phase produced by oxygen segregation. A characterisation of this phase by X-rays photoemission spectroscopy and high resolution electron energy loss spectroscopy is given, from which we deduce that it extends several layers deep into the volume. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Oxygen interaction with Ag surfaces has attracted much attention over the past decades because of the unique selectivity of Ag powders for the catalytic reaction of ethylene to ethylene oxide (EtO). However, in spite of the great efforts spent in different laboratories in studying this system [1–4], no EtO formation was ever observed under controlled ultra-high vacuum conditions and both the underlying reaction mechanism and the reactive oxygen species escaped so far understanding and identification. Some papers pointed out a possible role of subsurface oxygen for the origin of the pressure gap [6]. Oxygen migration into the volume of the crystal is known to take place when
exposing Ag(110) to O$_2$ above 470 K [5], but the mechanism allowing for the incorporation of a large amount of oxygen into Ag samples remained unexplained. More recently it was shown that the Ag surface can be activated for the ethylene epoxidation reaction by exposing polycrystalline foils to mixtures of CO and O$_2$ as well as C$_2$H$_4$ and O$_2$ [7], yielding a not better characterised surface modification. An active role of subsurface oxygen is supported also by theory, which demonstrates that the barrier for the EtO production is strongly reduced when subsurface sites are occupied by oxygen atoms [8].

Subsurface migration of oxygen is particularly important for the Ag(001) surface [9]. The O/Ag(001) system was thoroughly investigated by the Genoa group in the last years [10–13]. Two different oxygen adatom phases, stable respectively below and above room temperature (RT), were discovered and characterised by high resolution electron energy loss spectroscopy (HREELS) and X-rays photoemission spectroscopy (XPS), including photoelectron diffraction analysis [10]. CO oxidation takes place only for the high temperature phase. After the reaction and upon further exposure to CO, the photoemission intensity close to the Fermi level, $E_F$, grows because of the formation of a surface oxide layer [12], with oxygen both above and below the surface. This phase is generated by oxygen segregation from the bulk induced either by transient CO adsorption above RT or by heating a CO covered surface to RT to activate oxygen mobility. In both cases CO acts as a chemical pump, stabilising the dissolved oxygen atoms in the near surface region and favouring their accumulation and the formation of the surface oxide.

In the present paper we give a more complete account of this phenomenon, showing in particular that oxygen can populate subsurface sites even from the gas phase provided channels connecting surface and subsurface region are formed by CO oxidation. No significant EtO production was however detected in ethylene oxidation experiments performed on the surface oxide phase. Surface modification might therefore be an important condition, yet not sufficient, to ignite the reaction.

2. Experimental

The XPS experiments were performed at the SuperESCA beamline of the ELETTRA Synchrotron Radiation Facility in Trieste, while the HREELS investigation was done in the laboratory of Genova. Details on the SuperESCA beamline and on the XPS apparatus can be found in Ref. [14], while the HREELS experimental set-up is described in Ref. [15].

In all experiments high purity O$_2$ (N50) and CO (N35) gases were dosed by backfilling the chamber up to a pressure of $5 \times 10^{-6}$ mbar. After dosing the pressure dropped below $5 \times 10^{-10}$ mbar in a few minutes.

Most XPS spectra were recorded at an emission angle of 40° from the surface normal, corresponding to grazing incidence of the photons and to near normal polarisation. Two different beam times were dedicated to the experiments reported in the present paper. As discussed in Ref. [12] the dissolved oxygen content was different in the two cases. For the experiments performed on the dissolved oxygen rich sample, we used photon energies $h\nu = 650$ eV for the O(1s) region, $h\nu = 430$ eV for the C(1s) region and $h\nu = 215$ eV for the valence band region. For the experiments performed on the dissolved oxygen depleted sample we worked with $h\nu = 655$ eV for the O(1s) region, $h\nu = 395$ eV for the C(1s) region and $h\nu = 182$ eV for the valence band region. These photon energies were chosen in order to maximise surface sensitivity and intensity of the photoelectron peaks. Given the photoemission cross section [16] and a photon flux twice as large at 395 eV than at 430 and 650 eV, the sensitivity for C is 3.2 times larger than for O for the experiments performed on the dissolved oxygen poor sample and two times smaller for the dissolved oxygen rich sample. The photoemission spectra in the valence band region were normalised to the secondary electron background at 30 eV below $E_F$.

The HREELS experiments were performed with a self-constructed spectrometer with rotatable monochromator, which allows to select the desired momentum transfer. The resolution was degraded to 20 meV in order to measure surface plasmon losses with a reasonable signal-to-noise ratio. The
angular acceptance at an incident electron beam energy of 16 eV was 2°, corresponding to an integration in reciprocal space of about 0.04 Å⁻¹. The surface plasmon dispersion data were recorded along the (100) direction.

The Ag samples were discs of 10 mm diameter and 3 mm thickness, oriented to within 0.1° from the nominal (0 0 1) plane. Before each experiment the surface was prepared by sputtering and annealing cycles, checking surface order by low energy electron diffraction (LEED) and surface cleanliness by XPS or by HREELS and Auger electron spectroscopy (AES) in Trieste and in Genova, respectively. Surface contamination was checked accurately also after the CO oxidation experiments, excluding in particular that the extra intensity close to $E_F$ might be due to CO induced segregation of transition metals.

3. Data presentation and discussion

3.1. Oxygen segregation

In a previous paper [10] we demonstrated that oxygen atoms adsorb on the bare Ag(0 0 1) surface in three different moieties, characterised by O(1s) binding energies, $E_B$(O(1s)), of 530.3 eV (O530), 528.3 eV (O528) and 529.0 eV (O529), respectively. The first species corresponds to adatoms on a missing row reconstructed surface and it is stable for crystal temperatures, $T$, lower than 300 K. The second one consists of adatoms in fourfold hollows of a dereconstructed substrate restored for $T > 300$ K. The third moiety corresponds to a surface oxide phase observed after CO oxidation of O528 (the only species reactive towards CO oxidation). Subsurface oxygen is moreover present and characterised by a broad peak at $E_B$(O(1s)) > 530.5 eV. It was shown that transient CO adsorption leads to its segregation and to the formation of a surface oxide phase, characterised by a high density of states (DOS) at 0.8 eV below the Fermi level, $E_F$ [12]. The process occurs however only after O528 is removed by CO oxidation, leaving active sites at which subsurface oxygen can segregate to the surface and through which it can emerge and form the surface oxide phase. The photoemission intensity at 0.8 eV below $E_F$ differed by one order of magnitude between the two beam times devoted to this experiment. The difference was ascribed to the different content of dissolved oxygen of the samples used in the experiments.

In Fig. 1 we show that on a crystal with a small dissolved oxygen content the surface oxide phase can be grown by dosing O₂ from the gas phase, rather than by segregation from the bulk. The process occurs however only if the relevant active sites have been previously created by CO oxidation.

Photoemission spectra are shown for the clean surface (continuous lines), the O528 covered surface (dotted lines), the same surface after removing O528 by CO oxidation at $T = 360$ K (dashed lines) and after subsequent exposure to 33 000 L of O₂ at $T = 490$ K (dot-dashed lines). The valence band region is reported in the upper panel, the O(1s) region in the lower one. The C(1s) region (not reported) remained always unstructured, indicating the absence of appreciable contamination by carbon containing species. For clean Ag(0 0 1) little intensity is present in the valence band region above the Ag(4d) bands. The O528 phase was prepared by dosing 3150 L of O₂ from the gas phase at $T = 150$ K to maximise the dissociative sticking coefficient (see Ref. [10]) and subsequent annealing to 360 K. The O(2p) antibonding peak at $E_B = 2.0$ eV and the O(1s) peak at 528.3 eV are evident in the XPS spectra. Both features disappear upon CO exposure at $T = 360$ K, indicating that O528 is removed by CO oxidation (dashed curves). The extra intensity just below the Fermi edge witnesses the early stage of the formation of the same surface oxide phase described in Ref. [12]. Such feature is weaker than the one observed after a similar treatment on a dissolved oxygen rich sample, so that the O(1s) peak at 529 eV is too faint to be observed. When the so-obtained surface is exposed to a massive dose of O₂ (33 000 L) at $T = 490$ K faint peaks form at 529.3 and 531.2 eV and the DOS below $E_F$ increases strongly and becomes clearly peaked around $E_B = 0.7$ eV. The energy of the last feature, slightly lower than the one obtained on a dissolved oxygen rich sample, shifts to 0.8 eV after annealing the surface to 570
K (see Fig. 3). As shown theoretically in Ref. [12], oxygen must be present both in the surface and in the tetrahedral subsurface sites.

When dosing a similar amount of oxygen on a surface, which had not been pre-treated by removing O$_{528}$ by CO oxidation, no surface oxide forms, as demonstrated by the experiment reported in Fig. 2. After exposing bare Ag(001) to 86 400 L of O$_2$ at $T = 500$ K (dotted curves) only the O$_{528}$ related peaks are observed (at 528.0 eV in the O(1s) region and 2.0 eV below $E_F$ in the valence band region). From the intensity of the O$_{528}$ O(1s) peak we can infer a surface coverage of $\approx 0.1$ ML, corresponding to an average sticking coefficient close to $10^{-6}$. The outcome of the experiments of Figs. 1 and 2 shows therefore a
dramatic difference, which cannot be explained by the different exposures: in the latter case oxygen adsorbs in the O528 phase; in the former, on the contrary, it occupies also subsurface sites and is organised in the subsurface oxide phase, as witnessed by the doublet at 529.3 and 531.2 eV and by the increased DOS below $E_F$. The surface modification induced by CO oxidation has therefore opened diffusion channels through which oxygen adatoms can migrate to subsurface sites.

In the upper panel of Fig. 3 we show the crystal temperature dependence of the extra DOS below $E_F$ for the surface oxide phase obtained in the experiment of Fig. 1. After flashing the crystal to 570 K the feature becomes sharper. This intensity eventually decreases upon annealing to 620 K and disappears below 670 K. A peak at $E_B = 2.3$ eV, without its companion at 528.3 eV, is then present and can be completely eliminated only by ion bombardment. In the O(1s) region (lower panel) we initially observe intensity at 529.3 and 531.2 eV. When flashing to 670 K such peaks merge into a single peak at 530.2 eV. The C(1s) region (not shown) was monitored to check for possible carbon contamination, but again no C peaks were observed. The DOS at $E_B = 2.3$ eV is therefore due to atomic oxygen. However it cannot be due to O528, as no intensity is present at $E_B = 528.3$ eV, nor to O530, as it would be unstable at $T = 670$ K and the O(2p) antibonding structure would be present at 3.0 eV [10]. An O(2p) binding energy of 2 eV might be appropriate for oxygen in octahedral subsurface sites [17], which would then be populated as the result of the dissolution of the surface oxide phase. An oxygen moiety with $E_B = 530.5$ eV and stable up to high temperatures was reported also by Muhler and co-workers [4] after O$_2$ exposure on Ag(111) at atmospheric pressure and was assigned to subsurface oxygen. This behaviour is at variance with what observed for the dissolved oxygen rich sample, for which the DOS below $E_F$ persisted when heating to the same temperature [12].

In order to better characterise the surface oxide phase we studied the dependence of the peak at 0.8 eV on photon energy, $h\nu$, and on azimuthal orientation. In Fig. 4 we report XPS spectra of the valence band region recorded for the dissolved oxygen rich crystal and normalised to the energy loss tail at 30 eV. In panel A spectra recorded at $h\nu = 215$ eV for clean Ag(001) and for the surface oxide phase are compared. The modification affects shape and intensity of the Ag(4d) bands. Inspection of the Ag(3d) levels was performed only
for the surface oxide phase on the dissolved oxygen depleted sample (conditions of the experiment of Fig. 1) and shows a shift of 70 meV towards larger $E_B$ values. No evident change in their shape was observed. However for this surface the change was small also for Ag(4d). In panel B XPS spectra of the modified surface are reported for different $h\nu$. The intensity at 0.8 eV increases with decreasing photon energy in the investigated range (down to 180 eV). Since it is quite weak when photoemission is excited by HeI radiation ($h\nu = 21$ eV), the maximum of the cross section must lie some-
where in-between. This behaviour is at odds with the one expected both for s and d electrons of Ag (see inset in Fig. 4, panel B) so that s–d hybridisation must have occurred. This finding agrees with the assignment of the photoemission intensity below $E_F$ to orbitals generated by the interaction of the antibonding states associated to the O(2p) level of adatoms and subsurface atoms with the Ag(4d) bands [12]. The peak intensity is largest along the (100) direction, as shown by the difference spectra (modified surface minus bare surface, recorded at $h\nu = 215$ eV) reported in Fig. 5. We note that the extra density below $E_F$ compensates approximately the decrease in intensity of the Ag(4d) bands, in accord with its partial d-character.

Fig. 6 shows the comparison between the shape of the peak at 0.8 eV of the experiment in Fig. 3 (left panel, continuous line) and the one produced on a dissolved oxygen rich Ag(001) sample by dosing CO on O528 [12] (right panel, continuous line). The higher dissolved oxygen concentration makes the mechanism for the formation of the surface oxide phase more efficient, and the intensity of the resulting feature is 10 times larger (note the scale factor and the larger cross section at 186 eV (see Fig. 4)). The identical shape of the two peaks proves however that the surface oxide phase is the same, independently of the way by which oxygen is provided. After annealing to 670 K (dashed lines) the peak at $E_B = 0.8$ eV disappears.
in the present experiment while it survived with a reduced intensity for the dissolved oxygen rich sample. The intensity around 2.3 eV might then be present, too, but hidden by the oxide peak.

3.2. Effect on surface reactivity

Like CO, also ethylene reacts appreciably only with O528, leading to total oxidation, but no enhancement of the DOS below $E_F$ could be detected after this process. The surface modification takes therefore place efficiently only with CO in contrast with the previous finding by Bukthyarov et al. [7], who reported that O$_2$ and C$_2$H$_4$ mixtures work as well when exposing in the mbar pressure range.

The effect of the surface oxide phase on surface reactivity is shown in Fig. 7 for the dissolved oxygen poor sample. The modified surface is exposed to CO at 117 K. The initial situation (continuous line) is characterised by the structure at $E_B = 0.8$ eV in the valence band region (panel A) and by the broad feature between 530 and 533 eV in the O(1s) region (panel B), which witnesses the presence of the surface oxide phase. Carbon contamination is negligible, as demonstrated by inspection of the C(1s) region (panel C). After dosing 8000 L of CO at 117 K and flashing to 173 K to remove some co-adsorbed H$_2$O (dashed curves), the DOS just below $E_F$ grows and, more importantly, a feature forms at $E_B = 3.3$ eV. Such peak and the companions at $E_B = 533.0$ eV in the O(1s) region and at $E_B = 286.7$ eV in the C(1s) region are fingerprints of stable CO adsorption and correspond to the CO species desorbing at $T > 163$ K reported in Ref. [12]. After annealing above 220 K (dotted lines) the CO related features have disappeared, while the intensity in the valence band region just below $E_F$ increases with respect to the initial condition. On the contrary, if the same CO dosing experiment is performed on the bare or on the O530 pre-covered surface, no stable CO adsorption is observed. CO stabilisation is therefore connected to the presence of oxygen in subsurface sites. However this oxygen does not need to be organised in the surface oxide phase, since CO adsorption was observed at $T = 130$ K for a dissolved oxygen rich sample also prior to the formation of the structure at 0.8 eV [12]. The presence in those conditions of a peak at $E_B = 2.3$ eV without the counterpart at 528.3 eV (observed also...
after heating the modified surface (see Fig. 3)) is suggested by LDA calculations to correspond to oxygen atoms in octahedral interstitial sites [17]. We did not find appreciable effects of the surface modification for \( \text{C}_2\text{H}_4 \) oxidation. In particular ethylene adsorption is not significantly stabilised for the modified surface and no EtO production was detected in \( \text{O}_2 \) and \( \text{C}_2\text{H}_4 \) co-adsorption experiments in the investigated temperature range. This negative result does however not rule out a possible role of the surface oxide phase in the partial oxidation process under industrial conditions, as EtO formation could be inhibited by the presence of energy barriers which cannot be overcome in our experimental conditions.

3.3. Surface plasmon dispersion

Further information on the surface oxide phase induced by transient CO adsorption can be gained from the investigation of the surface plasmon losses. HREEL spectra at vanishing momentum transfer, \( q = 0 \), are reported in Fig. 8 for the O528 covered surface (lower spectrum) and for the phase resulting from the exposure of the O528 phase to 1600 L of CO (upper spectrum). The initial coverage of O528 is estimated from the HREELS intensity of the O–Ag vibration to be 0.1 ML and CO was dosed at \( T = 385 \) K; the experimental conditions are thus similar to those of the experiment of Fig. 1. We find that for the surface oxide phase the surface plasmon loss is shifted by 40 meV towards higher frequencies with respect to clean Ag(001). For the oxygen covered surface, on
the contrary, the frequency is unaffected in agreement with classic dielectric theory [18], which states that the surface plasmon energy is determined by the bulk dielectric function, while surface plasmon dispersion depends on surface properties.

The data for the surface oxide phase are collected vs. $q_k$ in Fig. 9: the triangles correspond to the O528 phase and were taken from Ref. [18], the dashed line is the result for bare Ag(001) [19], while the circles are the values measured for the surface oxide phase. The linear best fit to the data is also shown and the so-determined coefficients are collected in Table 1 and compared with clean and oxygen covered surface. As one can see, the frequency shift of the surface plasmon loss is nearly uniform over reciprocal space so that the linear dispersion is preserved with nearly the same slope as for the surface covered by oxygen adatoms. This finding is indicative that oxygen adatoms are still present at the surface after the oxidation process.

The shift of the surface plasmon frequency cannot be instrumental. Indeed if it were due to convolution over a larger portion of reciprocal space (caused e.g. by increased surface disorder), at large $q ||$, a decrease rather than an increase of the apparent loss frequency would be expected. On the other hand, a change at the surface would affect only the dispersion [19] and not the frequency at $q_0 = 0$. The only possible conclusion is therefore that the modified surface layer extends deep enough into the bulk to form a film with different dielectric properties from bulk Ag. \(^1\) This conclusion is consistent with the oxygen segregation mechanism for the production of the modified surface layers.

4. Conclusions

In conclusion we have characterised the surface oxide phase which forms on Ag(001) when oxygen adatoms of the O528 species are removed by CO oxidation, by studying the photon energy dependence of the XPS photoemission intensities and the surface plasmon frequency and dispersion. We find that (i) the modification extends deep into the bulk, in accord with the proposed mechanism of its formation by segregation of dissolved oxygen [12]; (ii) CO oxidation of O528 is a necessary step for the formation of channels linking surface and subsurface regions. If the oxygen concentration in the bulk is large, CO acts as a chemical pump by stabilising the mobile oxygen atoms in the surface region. Otherwise oxygen can be provided from the gas phase by dosing O2 and the surface oxide phase forms by accumulation of oxygen atoms penetrating through the channels into the subsurface region.

\(^1\) More precisely, at wavelengths larger than the thickness of the film the surface plasmon energy is expected at the value determined by the bulk dielectric properties of the substrate. The corresponding $q_k$ cannot be investigated by HREELLS because of the finite angular acceptance of the spectrometer.
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References