XPS, UPS, TPD and TPR studies of oxygen species active in silver-catalysed ethylene epoxidation

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The covalent oxygen chemisorbed on silver has been characterised by XPS, UPS, TPD and TPR. It has been shown that this oxygen species active in ethylene epoxidation is characterised by full isotope scrambling in TPD spectra of O_2 and the absence of UPS lines located below the silver 4d zone. Both the results testify its atomic origin.

Keywords: silver, oxygen, ethylene, epoxidation, isotope, photoelectron spectroscopy, temperature-programmed desorption

1. Introduction

The long-standing interest in the study of oxygen chemisorption at silver surfaces ([1] and references therein) has been stimulated by attempts of researchers to identify whichever of oxygen species is responsible for the ethylene oxide production as opposed to the formation of by-products (CO_2 and H_2O) governed by the oxide-like species, O^{2-}. There are two principally distinctive concepts [2–8]. One of them [2–4] connects the epoxidation route with molecularly chemisorbed oxygen, while the second hypothesis [5–7] suggests the active role of atomic oxygen. For a long time, both concepts have been under discussion. However, the appearance of papers, the authors of which have observed ethylene oxide ($m/z = 29$) among the products of temperature-programmed reaction (TPR) of ethylene with atomically chemisorbed oxygen, has compelled most followers of the molecular oxygen hypothesis to change their opinion. Moreover, special efforts have been undertaken by Grant and Lambert [6] in order to prove that the molecularly chemisorbed oxygen does not play a direct role in epoxidation. The same conclusion about an atomic origin of the epoxidising oxygen has been made in our previous papers [7,8] where treatment of silver foil with the reaction mixture has been used to activate it for ethylene epoxidation.

However, the molecular oxygen hypothesis has got a new stimulus for discussion by recent papers of Boronin et al. [9,10], who have characterised so-called covalent oxygen by ultraviolet photoelectron spectroscopy (UPS). They have shown that the formation of this oxygen species, active in ethylene epoxidation [8], is accompanied by the development of lines in UPS spectra with binding energies of 7.9, 9.6 and 12.8 eV below the Fermi level. Taking into account the data of Martin and Hey [11] and Rösch and Menzel [12] that the atomic oxygen produces an emission band in the range 0–6 eV below the Fermi level, the authors have concluded a molecular origin of the epoxidising oxygen.

It should be, however, noted that this assignment seems to be rather speculative. Indeed, the reaction conditions [9] used for the formation of this oxygen were severe enough to modify the subsurface silver layers by carbon- and/or oxygen-containing species [7]. Since ultraviolet photoelectron spectroscopy is not a fingerprint method for oxygen adsorbed at surfaces, it is clear that the UPS lines revealed in [9] can belong to these subsurface species, but not to chemisorbed oxygen. Obviously, other methods allowing one to obtain more unambiguous (conclusive) data should be used for this purpose. One of these is the analysis of TPD spectra taken after adsorption of isotope-labelled O_2. Indeed, if an equimolar mixture of $^{16}O_2$ and $^{18}O_2$ chemisorbs molecularly, then no isotope scrambling takes place at following heating the surface: only “masses” (m/z) of 32 and 36 are observed in the TPD spectra of O_2 [13–15]. In contrast to this, dissociative adsorption of O_2 molecules causes full mixing of isotopes. As a consequence, the corresponding intensity ratios of the TPD peaks will be equal to $1:2:1$ for $^{16}O_2$ ($m/z = 32$)/$^{16}O^{18}O$ ($m/z = 34$)/$^{18}O_2$ ($m/z = 36$), respectively [13–15]. However, a masking effect of O_2 evolving in TPD experiments due to desorption of the subsurface oxygen made it impossible to use the TPD isotope experiments to check the nature of the epoxidising oxygen produced in [7–9].

In this paper, we tried to select the conditions allowing us to avoid the formation of subsurface species and, at the same time, to prepare the epoxidising oxygen. This is necessary to measure the O_2 TPD spectrum of this oxygen. We show that decrease in the temperature of treatment and concentration of ethylene in $C_2H_4 + O_2$ mixtures provides disappearance of TPD peaks characteristic of the subsurface oxygen and, as a consequence, observing the TPD peaks of the epoxidising oxygen. Subsequent experiments with

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an equimolar mixture of $^{16}O_2$ and $^{18}O_2$ determines isotope scrambling conclusive of atomic origin of this oxygen. In full accordance with these data, the UPS spectrum of such non-modified surface does not exhibit any peaks with BE higher than 7 eV.

2. Experimental

All the experiments were carried out with a VG ESCALAB high-pressure electron spectrometer. This spectrometer was equipped with XPS, UPS, TPD and argon etching [16,17]. Treatments at “high pressure” ($P > 1$ Pa) were performed in the preparation chamber. The subsequent evacuation and transfer into the analyser chamber take about 3 min. The use of high pressures of reaction mixtures (up to 10^3 Pa) for silver modification necessitated control of the following potential problems: (i) gas evolving from component parts of the sample holder during TPD, and (ii) formation of carbonates on the silver surface. To tackle the former problem we have conducted blank experiments which have shown an absence of any gas evolving from the empty holder up to $\sim$800 K. To prevent the accumulation of carbonates we have held the sample temperature of 420 K during the recording of XPS spectra (420 K is high enough to decompose the carbonates and low enough for the adlayers of oxygen to be stable). Carbonates were controlled by recording C 1s spectra and TPD spectra of CO_2 after each treatment of Ag.

A polycrystalline silver foil (99.99%) was used for the investigation. A specially designed holder with independent heating of the sample was designed to avoid any gases evolving from the holder details during TPD even after high-pressure treatment. The scheme of Ag foil mounting on the sample holder is shown in figure 1. The sample heating was performed by passing a current through tungsten wires spot-welded to the backside of the Ag foil. The temperature of the sample was measured by a Pt–Pt/Rh thermocouple spot-welded also to the back of the foil. Such construction enables us to heat the sample with heating rate up to 10 K/s and to take away the sample holder details from the XPS analysis zone. The latter is necessary to apply electron spectroscopy and thermodesorption mass spectrometry together. Cleaning the silver surface was effected by cycles of ion etching followed by O_2 adsorption and flashing in vacuum up to 900 K.

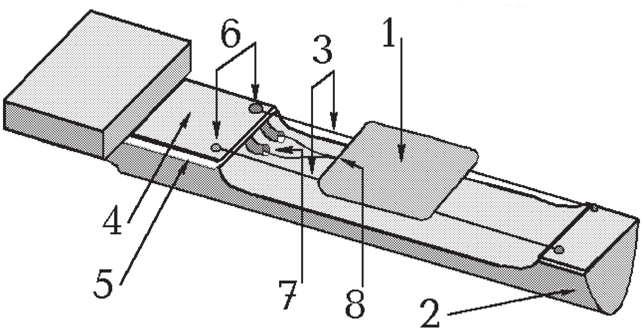

Figure 1. The scheme of sample mounting on holder with independent heating of the sample: 1 – sample, 2 – holder, 3 – tungsten wires, 4 – feedthroughs, 5 – insulating ceramic, 6 – spot welding, 7 – quartz capillaries, 8 – thermocouple.

XPS spectra were taken using Mg Kα irradiation and calibrated against BE(Ag $3d_{5/2}$) $=$ 368.1 eV. TPD spectra were recorded using a VG Q-7/B mass spectrometer. The reactivities of the adsorbed oxygen species towards C_2H_4 were studied by temperature-programmed reaction (TPR) spectroscopy, i.e., by means of the mass spectrometric analysis of the reaction products evolving upon the heating of the sample after ethylene adsorption at room temperature and $P(C_2H_4) = 10$ Pa [7,8]. We monitored the masses characteristic of CO_2 ($m/z = 44$), C_2H_4O ($m/z = 29$), C_2H_4 ($m/z = 27$), CO ($m/z = 28$), and O_2 ($m/z = 32$).

3. Results and discussion

Figure 2 shows (a) O 1s spectra and (b) TPD spectra of O_2 recorded after treatment of a clean silver polycrystalline foil with $C_2H_4 + O_2$ reaction mixtures under various conditions (the treatment conditions can be seen from the figure caption). The corresponding spectra recorded after O_2 adsorption at $T = 470$ K are also shown for comparison as dashed curves. One can see that the treatment of the clean surface with the reaction mixture provides the formation of the covalent oxygen with BE(O 1s) $=$ 530.5 eV (figure 2(a), curves 1, 2) as opposed to the well-known ionic oxygen with BE(O 1s) $=$ 528.4 eV (figure 2(a), dashed curve) which is produced as a result of adsorption of pure O_2. The use of $C_2H_4 + O_2$ instead of pure oxygen changes also the TPD spectra of O_2 (figure 2(b)). If the ionic oxygen, in full agreement with all literature data [13–15], desorbs as a narrow peak at $T_{\max} = 580$ K, so heating the surface treated with $C_2H_4 + O_2$ under the conditions used by us earlier [7] results in a wide TPD spectrum with constant growth of background intensity (figure 2(b), curve 1). Furthermore, an increase in time of the reaction mixture treatment enhances constantly the quantity of desorbing oxygen. At the same time the oxygen concentration measured by XPS reaches saturation (1 ML). These data indicate that this TPD spectrum originates from the desorption of dissolved oxygen which masks the TPD peak characteristic of the covalent oxygen.

To avoid the essential modification of subsurface silver layers by the dissolved oxygen and, as shown by us previously [7], by carboneous residues we decreased the temperature of the treatment and also diluted the gas mixtures with respect to ethylene. The same figure 2 presents the corresponding XPS and TPD spectra recorded after treatment of silver foil under milder conditions (figure 2, curve 2). Adsorption temperature of 420 K instead of 500 K, as well as $P(C_2H_4) : P(O_2) = 1 : 100$ partial pressure ratio (compare with $1 : 5$ [7,9]), was used for this experiment. One can see that like for the experiment with more severe conditions,

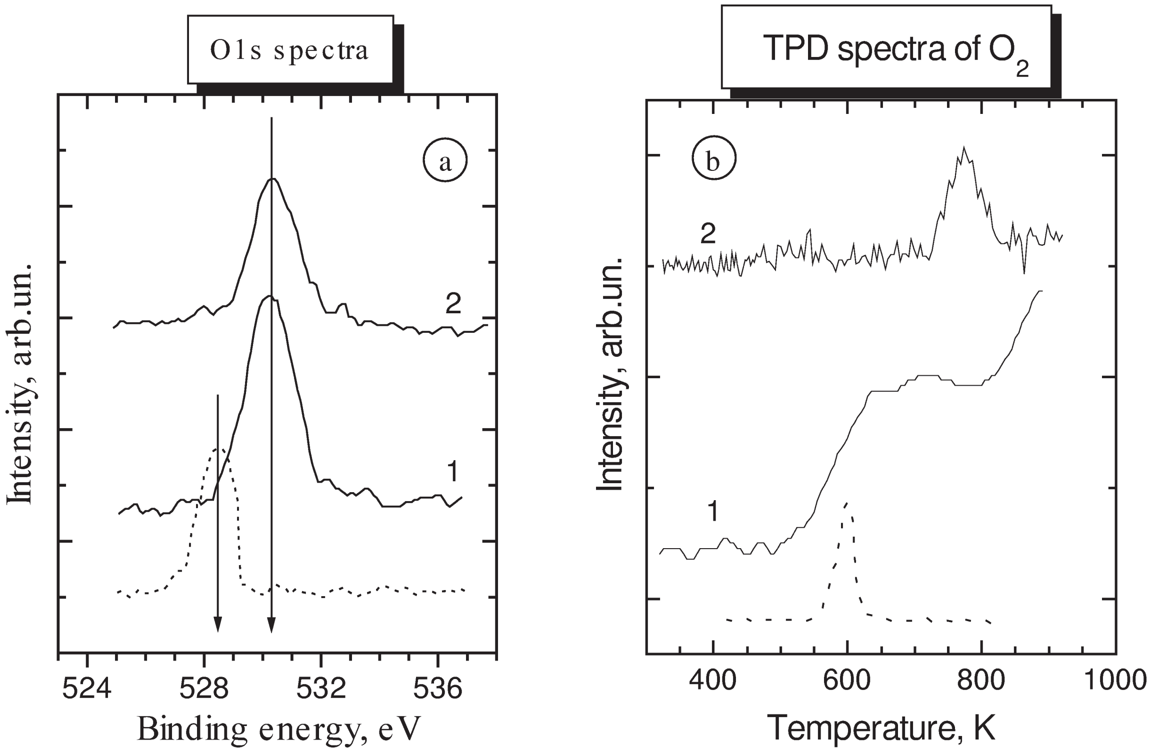

Figure 2. (a) O 1s spectra and (b) TPD spectra of O_2 recorded after treatment of the clean silver surface with $C_2H_4 + O_2$ reaction mixtures for 30 min under different conditions (1–2). (1) $T = 470$ K, $P = 1000$ Pa, $P(C_2H_4) : P(O_2) = 1 : 2$; (2) $T = 420$ K, $P = 100$ Pa, $P(C_2H_4) : P(O_2) = 1 : 100$.

this treatment with the reaction mixture provides the appearance of the O 1s line at 530.5 eV characteristic of the covalent oxygen. It should be, however, noted that the maximum intensity of this line becomes two times less than for more severe conditions (figure 2(a)) testifying the decrease in saturation coverage of the covalent oxygen. Furthermore, the use of milder conditions causes sharp changes in the shape of the TPD peaks (figure 2(b)): the broad desorption peak for O_2 is replaced by a narrow peak at 770 K.

The assignment of the TPD peak of O_2 with $T_{\max} =$ 770 K to desorption of chemisorbed oxygen characterised by the O 1s line at 530.5 eV was checked by comparison of desorption spectra recorded using TPD and XPS simultaneously. Since TPD testifies the evolving of desorbing molecules into the gas phase and XPS characterises the removal of chemisorbed species from a surface, so coincidence of the temperature ranges of these processes means their relationship. To make this comparison in more detail, we have developed a special procedure of preparing the desorption spectra from XPS data. Experimentally, XPS allows one to register the change in O 1s intensity measured at some binding energy value, as the sample temperature increases. As a rule, the point with maximum XPS intensity is chosen for such analysis. Subsequent transformation of the experimental curve of the XPS intensity variation to desorption spectra includes the following mathematical operations:

(1) smoothing the measured experimental dependency of the O 1s intensity on temperature;

(2) differentiating the smoothed curve;

(3) inverting the differentiated curve according to the mathematical operation $(-Y)$.

In general, such procedure means the transformation of the curve of O 1s intensity variation to the differential curve of the rate of this variation and is justified by the fact that the “true” TPD spectrum of O_2 represents itself the rate of O_2 evolving into the gas phase. The first operation is necessary to avoid high signal-to-noise ratio of the differentiated curve, and the third one changes the sign which becomes positive for both curves.

Figure 3 presents the results of such experiment for the desorption of the ionic oxygen with BE(O 1s) = 528.4 eV. It is well known [7,10,14] that this oxide-like species desorbs at about 580 K, and this process is not accompanied by any processes (dissolution or transformation to other species followed by their desorption at other temperatures, etc.) which could affect XPS desorption curve and, hence, hinder its comparison with TPD spectra of O_2. Therefore, it was this oxygen which was used here as a model object to test the procedure described above. In full agreement with our expectations, the desorption spectrum of the ionic oxygen produced on the basis of XPS coincides with TPD spectrum of O_2 evolving recorded by mass spectrometry (figure 3(d)). This result confirms correctness of our method and its validity for checking the question whether the TPD peak of O_2 at 770 K reflects the desorption of the covalent oxygen or whether it originates from the escape of dissolved oxygen.

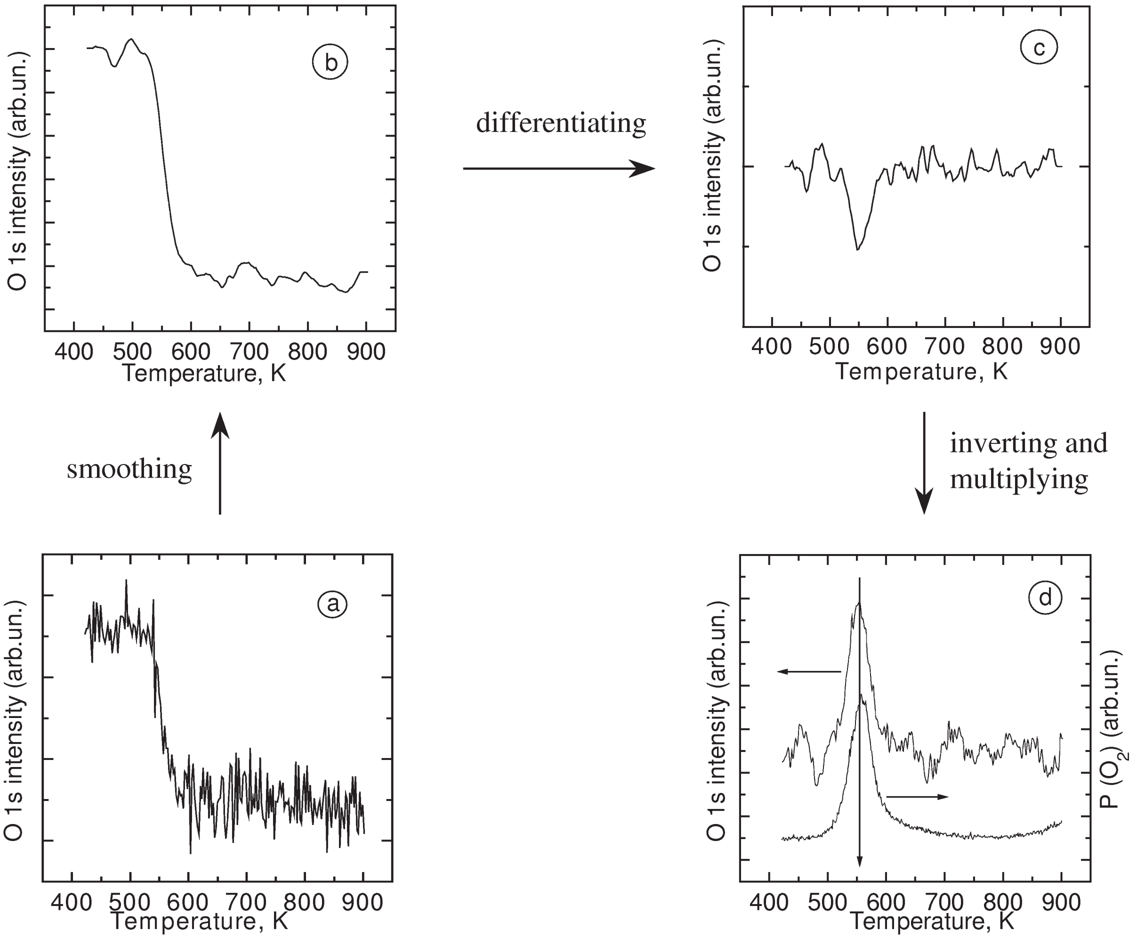

Figure 3. The procedure of preparing the desorption spectrum of the ionic oxygen (BE(O 1s) = 528.4 eV) on the basis of XPS data (see text).

The desorption curves measured for the covalent oxygen by mass spectrometry and by X-ray photoelectron spectroscopy are compared in figure 4(b). The O 1s spectrum recorded before desorption is also shown in this figure (figure 4(a)). One can see that the O 1s signal at 530.5 eV diminishes sharply in the temperature range of 720–800 K (figure 4(b), curve 2). Absence of any lines in the O 1s spectrum after heating up to 900 K demonstrates that the decrease in the O 1s intensity is due to disappearance of the covalent oxygen but not due to its transformation to another species with the distinctive binding energy of the O 1s line. The transformation of the O 1s intensity variation curve to a desorption spectrum results in the curve (figure 4(b), curve 2*) which coincides practically with the “true” TPD spectrum of O_2 evolving (figure 4(b), curve 1). Good coincidence of these desorption curves produced by surface-sensitive and gas-phase techniques (XPS and TPD, respectively) confirms the assignment of the TPD peak of O_2 at 770 K to the desorption of the covalent chemisorbed oxygen. This result is of great importance, since it indicates that the use of oxygen isotopes will be informative to check the origin of the covalent oxygen by TPD.

However, before carrying out these isotope experiments we have tested the reactivity of the covalent oxygen towards ethylene. It was necessary, since the conditions used in the present work for its formation were so mild that they allowed us to suppress the modification of the silver subsurface layer (figure 2(b), curve 2). It is obvious that such non-modified surface could lose its activity to epoxidise ethylene. To check the reactivity of the covalent oxygen towards C_2H_4, we have carried out unsteady-state TPR experiments. Preliminary, the surface with half a monolayer of the covalent oxygen has been exposed to molecular oxygen at $T = 420$ K and $P = 10$ Pa in order to produce the ionic oxygen with BE = 528.4 eV (figure 4(c)). This oxide-like oxygen has proved to be necessary to create the sites (Ag^+) for ethylene adsorption [8,18]. After adsorption of C_2H_4 at $T = 300$ K and $P = 10$ Pa on the surface containing two oxygen species, narrow peaks appear in the TPR spectra of CO_2 ($m/z = 44$) and of C_2H_4O ($m/z = 29$ [19]). This result indicates that despite the mild conditions of the covalent oxygen formation this oxygen species preserves its property to oxidise ethylene to ethylene oxide.

Thus, the use of mild conditions for the reaction mixture treatment of the clean silver surface allowed us not only to activate the surface for ethylene epoxidation, but also to exclude the formation of subsurface oxygen and, as a consequence, to measure the TPD peak of O_2 for the epox-

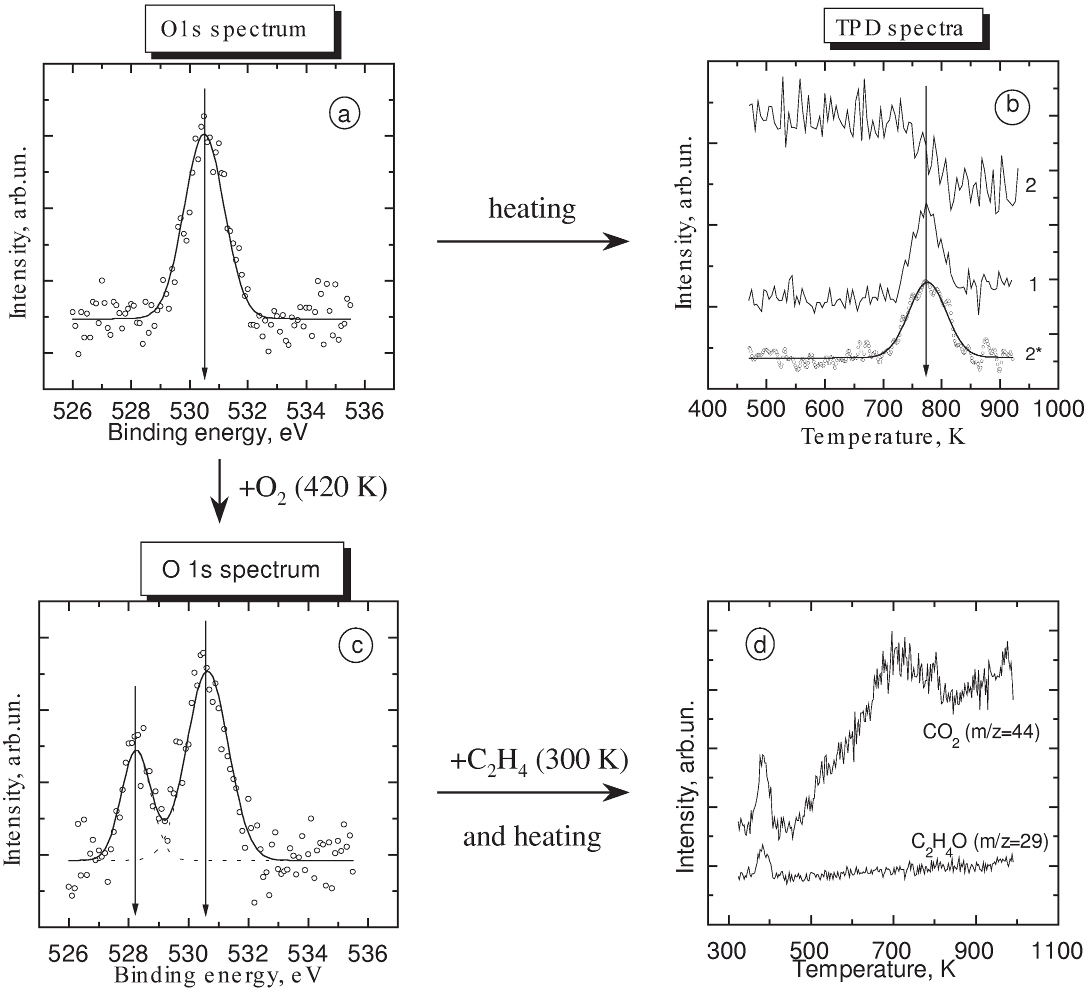

Figure 4. (a) O 1s and (b) TPD spectra of the covalent oxygen species produced by the reaction mixture treatment under mild conditions (see figure 2), as well as (c) TPR spectra of C_2H_4O and CO_2 from the surface with the covalent oxygen exposed to O_2 for 10 min at $T = 420$ K and $P = 10$ Pa, (d) followed by ethylene adsorption for 10 min at $T = 300$ K and $P = 10$ Pa.

idising species – the covalent oxygen. The latter makes it possible to carry out the isotope experiments. The results of such experiment are presented in figure 5 which shows TPD spectra of O_2 with $m/z = 32$ ($^{16}O^{16}O$), 34 ($^{16}O^{18}O$) and 36 ($^{18}O^{18}O$) recorded after treatment of the clean silver surface with an equimolar mixture of $^{16}O_2$ and $^{18}O_2$ (100 Pa for 1 h at 420 K), in which 1% of ethylene has been added. In full agreement with previous experiments (figures 2 and 4), such treatment produces the covalent oxygen which is testified by the O 1s line with BE = 530.5 eV and the TPD peaks of O_2 at 770 K (figure 4). One can see that the isotope composition of the desorbing oxygen, $1:2:1$ for $^{16}O_2/^{16}O^{18}O/^{18}O_2$, indicates the random scrambling of the isotopes. Mass-spectrometric control of the isotope compositions of the reaction mixtures during the treatment have not shown accumulation of $^{16}O^{18}O$ isotope into the gas phase, therefore we can conclude that the isotope scrambling occurs on the silver surface, but not on the walls of the spectrometer chambers. This result (full isotope scrambling) seems to indicate that the covalent oxygen has an atomic origin. Indeed, desorption of molecular oxygen both from low-temperature species ($T_{\max} = 170$ K) measured by Backx [13] and from high-temperature species ($T_{\max} = 380$ K) revealed by Grant and Lambert [15] was characterised the isotope ratios of $1:0:1$, i.e., O_2 molecules with isotope composition of $^{16}O^{18}O$ ($m/z = 34$) were absent in TPD spectra.

The conclusion about the atomic origin of the covalent O_{ads} is in agreement with our suggestion that the UPS peaks with BE below the silver 4d-band observed in [9] arise from subsurface oxygen-containing species, but not from molecularly chemisorbed species. Additional confirmation of this has been obtained by us from UPS spectra of the silver surface treated with the reaction mixture in the mild conditions, i.e., when the covalent oxygen is produced without essential modification of the silver. Figure 6 presents the valence band photoelectron spectrum of such surface, with the corresponding spectrum of the clean surface being also shown for comparison. HeII irradiation was used to take these spectra. One can see that, as opposed to Boronin's work [9], no peaks are observed located below the silver d-band in the corresponding difference spectrum. This result demonstrates that the UPS peaks with higher binding energies in [9] are most likely assignable to subsurface species with

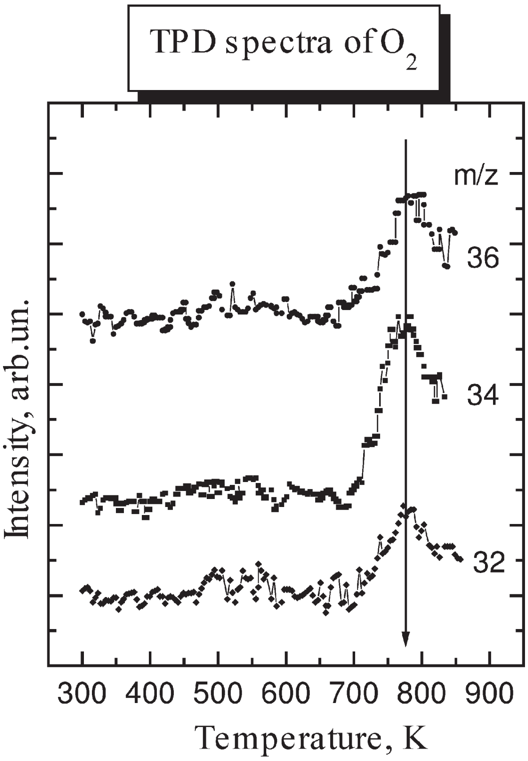

Figure 5. TPD spectra of O_2 with $m/z = 32$ ($^{16}O^{16}O$), 34 ($^{16}O^{18}O$) and 36 ($^{18}O^{18}O$) recorded after treatment of the clean silver surface with an equimolar mixture of $^{16}O_2$ and $^{18}O_2$ with 1% of ethylene at $T = 420$ K and $P = 100$ Pa.

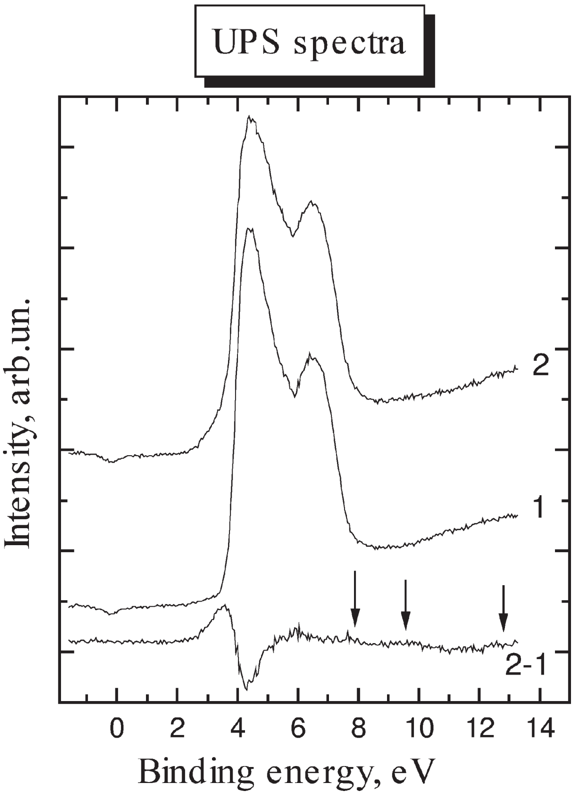

Figure 6. UPS HeII spectra recorded from the clean silver surface and from the silver surface with the covalent oxygen species. The difference spectrum is also shown for comparison.

a more complex composition than that of adsorbed oxygen. The comparison with literature data indicates that carbonate and hydroxyl groups should be recognised as the most possible candidates for explaining these UPS lines. Indeed, the UPS peaks at binding energies above the silver 4d-bands observed in [20,21] have been assigned to surface carbonate structures formed via reaction of oxygen chemisorbed at the silver surface with gas-phase CO_2 [10,22]. The assignment of UPS peaks with binding energies of 9.8 and 12.5 eV to hydroxyl groups produced on the silver surface as a result of high-pressure treatment has been made in the works of Schlögl and co-workers [23,24]. It is obvious that so severe conditions as those used in previous works [7,9] are reactive enough to form CO_2 and H_2O as products of total oxidation of ethylene, the appearance of which makes it possible to accumulate the species mentioned above. Furthermore, according to Schlögl's data [24] subsurface location of these species can increase the temperature of their decomposition and, hence, provides their stability in the conditions of spectra recording.

4. Summary

The use of $T = 420$ K and decrease in ethylene concentration in the $C_2H_4 + O_2$ reaction mixture during the treatment of a clean silver surface allowed us to avoid essential modification of subsurface silver layers by carbon and oxygen atoms and to produce the covalent species of chemisorbed oxygen. It has been shown that even in the absence of the subsurface modification the covalent oxygen preserves its capability to epoxidise ethylene. It exhibits random isotope scrambling in TPD experiments. This result testifies that this oxygen species has the atomic origin.

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