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Study of high-temperature oxygen states on the silver surface by XPS and UPS

A.I. Boronin, S.V. Koscheev, V.F. Malakhov and G.M. Zhidomirov

Federal Scientific Center, Boreskov Institute of Catalysis SB RAS, Novosibirsk 630090, Russia

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XPS and UPS methods have been used to study the nature of the oxygen states on silver. Three oxygen states with high $E_b(\mathrm{O1s}) = 530.5$ eV ($\mathrm{O_{epox}}$), 530.9 eV (O_β), 532.0 eV ($\mathrm{O_{res}}$) can be reliably attributed to different adsorbed species of quasimolecular oxygen. These states are characterized by an unusually high thermostability ($T > 800$ K) and a subsurface location.

Keywords: X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), oxygen states, silver surface, partial oxidation

1. Introduction

Silver is a unique catalyst for heterogeneous partial oxidation of ethylene and methanol [1,2]. Understanding of the nature of the adsorbed oxygen states is one of the central problems in the investigation of the reaction mechanism. At present, there are plenty of publications concerning different aspects of the adsorbed oxygen states [3–27].

All the oxygen states are usually classified in three main groups: atomic adsorbed oxygen ($\mathrm{O_{at}}$), molecular adsorbed oxygen ($\mathrm{O_{mol}}$) and oxygen dissolved in the bulk or subsurface region (O_β or $\mathrm{O_{ss}}$).

The formation of $\mathrm{O_{at}}$ on clean surfaces at $T < 500$ K is well established. $\mathrm{O_{at}}$ is characterized by $E_b(\mathrm{O1s}) = 528.1$–$528.5$ eV, the desorption temperature around 600 K and a high Ag–O bond ionicity [12–19]. This state is very reactive towards CO, H_2 and is responsible for complete oxidation.

Partial oxidation starts to be noticeable after the modification of the surface structure, bulk and subsurface layers. The modification of silver can be achieved by its treatment with the reaction mixture (RM) $C_2H_4 + O_2$ at $T = 450$–600 K [9,19]. Such treatment stimulates the penetration of oxygen and carbon into the bulk and subsurface regions. According to Grant and Lambert [9], van Santen et al. [1,10] and Gelbshtein et al. [11], the adsorbed atomic oxygen changes its chemical state during the silver modification giving rise to the activity in ethylene epoxidation.

Another explanation of the role of the surface modification has been reported in refs. [15–19]. In these papers, the formation of a new oxygen state with $E_b(\mathrm{O1s}) = 530.5$ eV as a consequence of the surface modification was reported. The authors showed that this oxygen was immediately incorporated in an ethylene molecule to form ethylene oxide. We denote this oxygen state as $\mathrm{O_{epox}}$. The role of $\mathrm{O_{at}}$ ($E_b = 528.5$ eV) is to stimulate Ag^{1+} sites for strong irreversible adsorption of ethylene. So, in our previous work a double site model of the active adsorption centre was proposed.

The main conclusion is that epoxidizing oxygen was proposed to be atomic with a low Ag–O bond ionicity (“covalent” oxygen) providing electrophilic oxygen properties. It is noteworthy that $\mathrm{O_{epox}}$ is much more thermostable ($T_p = 820$ K) than $\mathrm{O_{at}}$ ($T_p = 580$ K). The thermostable oxygen states were observed in works by Lambert [8], Haul et al. [22], Bowker et al. [7], Ertl, Schlögl and coworkers [23–26]. Deng et al. [27] showed the existence of thermostable surface and subsurface oxygen species as well as molecular oxygen participating in the partial oxidation of methanol.

We should also note that the residual oxygen is observed in all the cases during the cleaning of the silver surfaces before the following adsorption experiments, especially for polycrystalline surfaces. This oxygen state cannot be removed after several cycles of argon etching with following annealing in vacuum up to 1000 K. It is possible to obtain a clean surface only after prolonged work with a sample.

Thus, thermostable oxygen states play an important role in the oxygen–silver chemistry and catalytic processes of partial oxidation. Experimental data indicate the subsurface location of some thermostable oxygen states. It should be noted that these states are interpreted as atomic oxygen and their possible molecularity has not been considered before.

In this paper we present experimental results obtained by XPS and UPS methods. It is shown that the thermostable states of oxygen on silver are not only atomic. Reliable data proving the existence of an O–O chemical bond for thermostable oxygen states in the subsurface layers of silver are presented.

2. Experimental

A VG Escalab high-pressure electron spectrometer was used to record the photoemission spectra. X-ray photoelectron spectra (XPS) were taken at Al K_α radiation ($h\nu = 1486.6$ eV). Experimental resolution characterized by full width at half maximum (FWHM) of the $Ag3d_{5/2}$ line was 1.3 and 2.0 eV for analyzer pass energy of 20 and 50 eV, respectively. UP spectra were recorded with a helium discharge lamp, with two main resonance lines, HeI ($h\nu = 21.2$ eV) and HeII ($h\nu = 40.8$ eV), used.

Originally created software PSILON, CALC and standard graphic packages were used for data acquisition and analysis. A polycrystalline silver foil and a silver film obtained by thermal decomposition of silver oxide (Ag_2O) directly in the spectrometer were employed as samples for investigations. The polycrystalline foil was mounted on W wires, Ag_2O powder was pressed in a Ni net with small mesh. The sample heating was realized by passing a current through W wires or Ni net. The temperature was measured with a Pt–Pt/Rh thermocouple spotwelded to the backside of the foil or Ni net. The thermoregulator combined with an IBM PC computer controlled the sample temperature with high accuracy (± 1 K). Taking into account the possible diffusion of Ni atoms from the support to the surface and the influence on the oxygen states XPS was used not only for recording spectroscopic characteristics of the O/Ag system (O1s, O-KLL, VB, Ag3d and Ag-MNN lines). We recorded Ni2p regions with a high sensitivity in every measurement to be sure that the sample is free of Ni.

The silver foil was cleaned from carbon and sodium by cycles of Ar^+ etching, oxygen treatments at 770 K with subsequent annealing in vacuum at 1000 K. No contaminations were detected by XPS after several cycles of the cleaning procedure, only residual oxygen with E_b(O1s) around 531–533 eV was observed.

Silver oxide was prepared by a traditional chemical way. The sample was tested by X-ray diffraction. Main contaminations – elementary carbon and carbonates – were removed by usual heating of the sample to 420–470 K in vacuum [19]. This treatment results in the decomposition of carbonates and CO_2 desorption as well as combustion of carbon with oxygen from Ag_2O. This process was controlled by XPS used in a high sensitive mode. No alkaline metals were observed in the silver oxide.

Treatments with the gas mixture ($C_2H_4 + O_2$) were carried out in the preparation chamber of the spectrometer. The purity of the gases was controlled by a mass-spectrometer.

To prevent distortion of the XPS and UPS spectra in the regime in situ, the sample was grounded through a connection of the thermocouple with earth.

3. Results

O1s spectra, which characterize typical states participating in the ethylene epoxidation reaction are presented in figure 1. The O1s spectrum of the initial surface (figure 1a, curve 1) is a quite broad line around 531 eV.

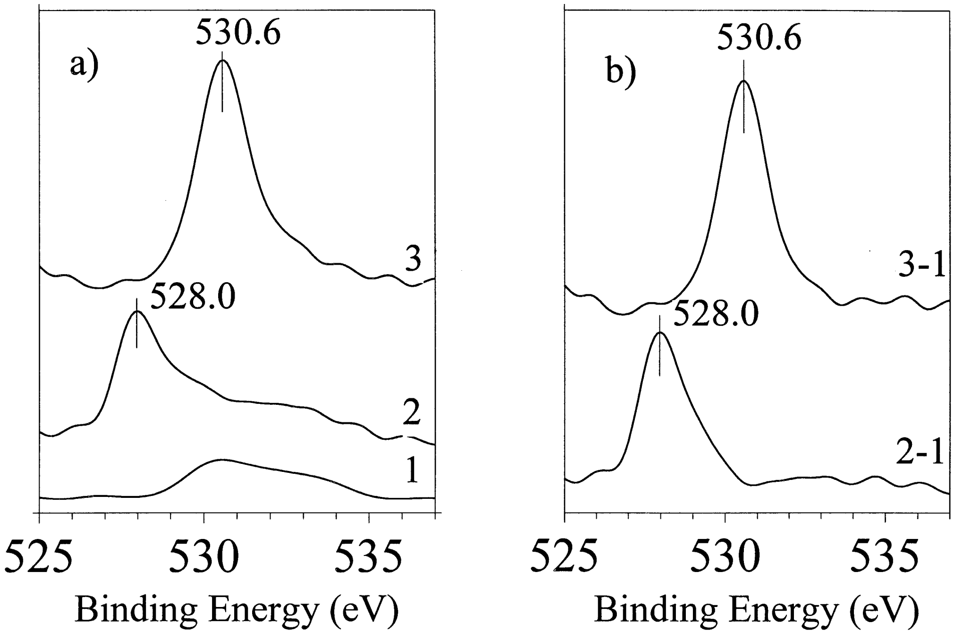

Figure 1. (a): (1) O1s spectrum of the initial polycrystalline surface after several cycles of the surface cleaning; (2) O1s spectrum obtained after the O_2 interaction at $T = 500$ K, $P(O_2) = 1$ Torr, 10 min, (3) O1s spectrum obtained after the action of the reaction mixture at $T = 500$ K, $P(C_2H_4)/P(O_2) = 1/5$, $t = 10$ min). (b): (2 − 1) the difference O1s spectrum (curve 2 minus curve 1 in (a)) characterizing the O_{at} state; (3 − 1) the difference O1s spectrum (curve 3 minus curve 1 in (a)) characterizing the O_{epox} state.

This is residual oxygen (O_{res}) which is unreactive towards CO, H_2, C_2H_4. Depending on the morphology, the sample history and the number of the cleaning cycles, the state of the residual oxygen can be characterized by E_b in the range of 529–533 eV with the coverage about 0.1–0.3 of a monolayer. The residual oxygen has a subsurface location. First, this state cannot be removed by the Ar etching only. Second, the thermal decomposition of Ag_2O (figure 2), where oxygen atoms are definitely in the bulk lattice location, results in a significant quantity of the residual oxygen, which does not desorb up to 1000 K, with $E_b = 530.5$–532.0 eV (figure 2, curves 2 and 3). Third, the residual oxygen does not prevent the following oxygen chemisorption from the gas phase, hence no blocking of the surface by the residual oxygen exists.

Figure 1b demonstrates the difference spectra 2 − 1 characterizing the first step of the oxygen adsorption on silver at 500 K. This state has $E_b = 528.2$ eV which indicates a high ionicity of the Ag–O bond in accordance with refs. [18,19]. All the literature data prove the atomic nature for this species. So, we denote this state as O_{at}. Also, the literature is unanimous in the opinion concerning its high reactivity but in only the complete oxidation.

The interaction with the reaction mixture (RM) ($C_2H_4 + O_2$) usually leads to the appearance of another oxygen state with $E_b = 530.5$ eV and coverage close to 1 ML. In figures 1a (curve 3), 1b (curve 3 − 1) typical O1s spectra obtained after the treatment by RM at 1 mbar ($P(C_2H_4/O_2) = 1/5$) are presented. In accordance with ref. [19], the formation of this state is accompanied by a strong modification of silver by dissolved oxygen and carbon. It was also shown that participation of both oxygen states is necessary for the ethylene epoxidation. O_{at} with $E_b = 528.2$ eV is responsible for the strong irreversible adsorption of ethylene at room temperature. The role of the oxygen state with $E_b = 530.5$ eV is to incorporate into the ethylene molecule thereby epoxidizing it. We call this state O_{epox}. This state "works" if there is strong irreversible (see above) adsorption of ethylene. If there is only one species (ionic atomic oxygen O_{at}) on the surface, only complete oxidation occurs, in accordance with all reference data.

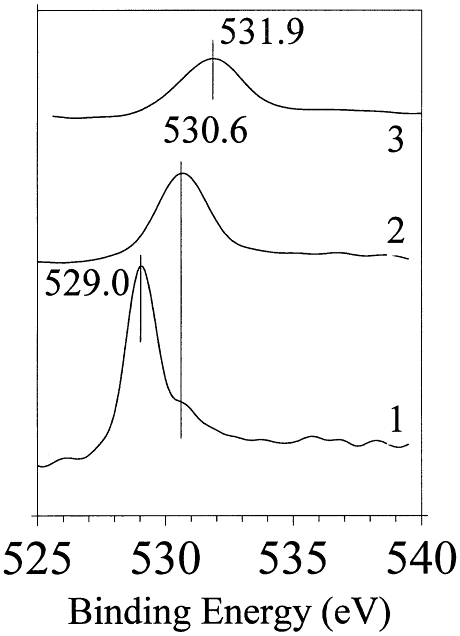

Figure 2. O1s spectra of Ag_2O surface after its cleaning from carbon–carbonate contaminations (curve 1) at $T = 420$ K and following annealing in vacuum at $T = 570$ K and $T = 1000$ K. All the spectra were recorded in situ.

Earlier O_{epox} was proposed to be atomic with a covalent character of the Ag–O bond [18,19]. This conclusion was made on the basis of the XP spectra, but data obtained by UPS do not confirm the above interpretation of O_{epox}. Figure 3 shows UPS spectra of O_{at} and O_{epox} corresponding to the XPS spectra presented in figure 1. From the difference UPS spectra one can see that the features belonging to O_{at} and O_{epox} are principally different. According to Prince et al. [33], the 4–7 eV range where the Ag4d band is located cannot be analyzed unambiguously, so we should consider the features only above and below the 4d band to make a correct interpretation. The formation of O_{at} results in a single feature above the 4d band with $E_b = 2.7$ eV while no noticeable changes in the 7–15 eV range are observed (figure 3a, curve 2 − 1). This experimental fact can be undoubtedly interpreted as atomic oxygen O_{at}, as we discussed above. The difference spectrum 3 − 1 in figure 3b (O_{epox}) has a much more complicated spectroscopic structure. In this case four positive peaks with $E_b = 3.4$, 7.9, 9.6 and 12.9 eV are observed in the difference spectrum. (As we shall see later, the fifth feature is located around 17–18 eV.) Usually, atomic oxygen adsorbed on metals produces an emission band near 5–6 eV. Calculations by Martin and Hay [30], and Rosch and Menzel [31] could give a bonding orbital feature around 7 eV. It is rather difficult to interpret a characteristics with $E_b > 7$ eV as an atomic oxygen. In any case, the spectroscopic structure observed cannot be interpreted as an atomic oxygen which is able to add one (bonding orbital) or two (bonding and antibonding orbitals) features [34] but not more.

Since the observation of the photoemission characteristics of epoxidizing oxygen in the range of 7–15 eV is a direct test on its molecular nature, it is very important to obtain additional confirmation that atomic oxygen cannot give any features at $E_b > 7$ eV. From this point of view we analyzed the photoemission (UPS) spectra of silver oxide Ag_2O (figures 4a and 4b, curve 1) where oxygen in the lattice is definitely atomic. The O1s spectrum of Ag_2O after removing carbon–carbonate contaminations is presented in figure 2 (curve 1). This spectrum is practically the same as the one obtained by Tjeng et al. [28] when they performed a detailed study of Ag_2O. As can be seen from figure 4b (curve 1) UPS indicates the

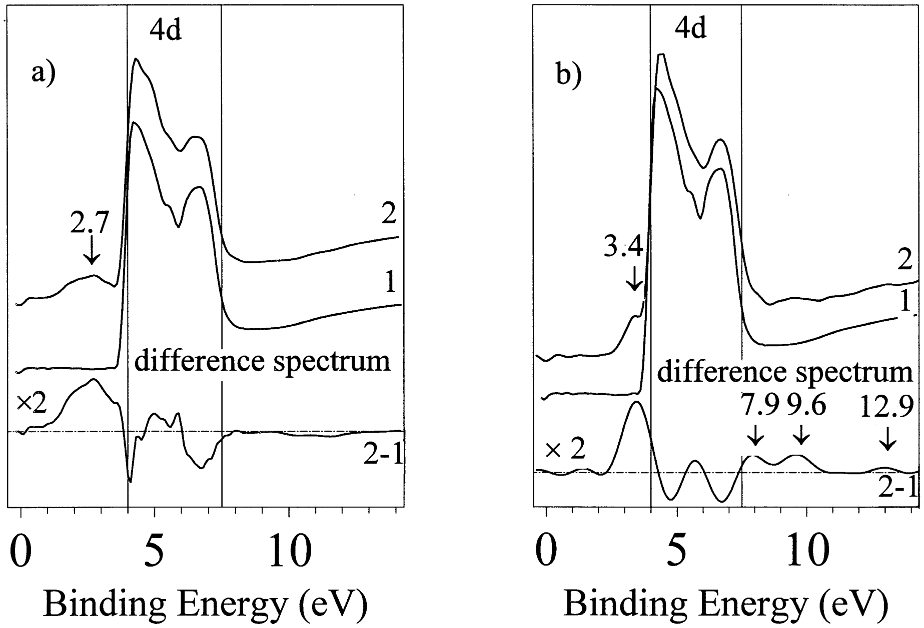

Figure 3. UPS He II spectra of the initial polycrystalline silver surface (a, b- curves 1); (a, b- curves 2) spectra obtained after the treatments with O_2 (a) and RM (b) which are identical to the treatments described in the caption of figure 1; (a, b- curves 2 − 1) the difference spectra (curves 2 minus curves 1).

photoyield from Ag_2O only in the range of 1–7 eV and no noticeable intensity deeper than 7 eV is observed.

Thus, UPS gives reliable evidence to consider the O_{epox} oxygen state ($E_b = 530.5$ eV) as a molecular oxygen, that is this oxygen species has an O–O bond.

It is noteworthy that O_{epox} is much more thermostable ($T_p = 820$ K) than another state O_{at} participating in the ethylene epoxidation ($T_p = 580$ K) [18,19]. In other words, UPS data create a new problem that oxygen states with quasimolecular (it is more correct to speak of

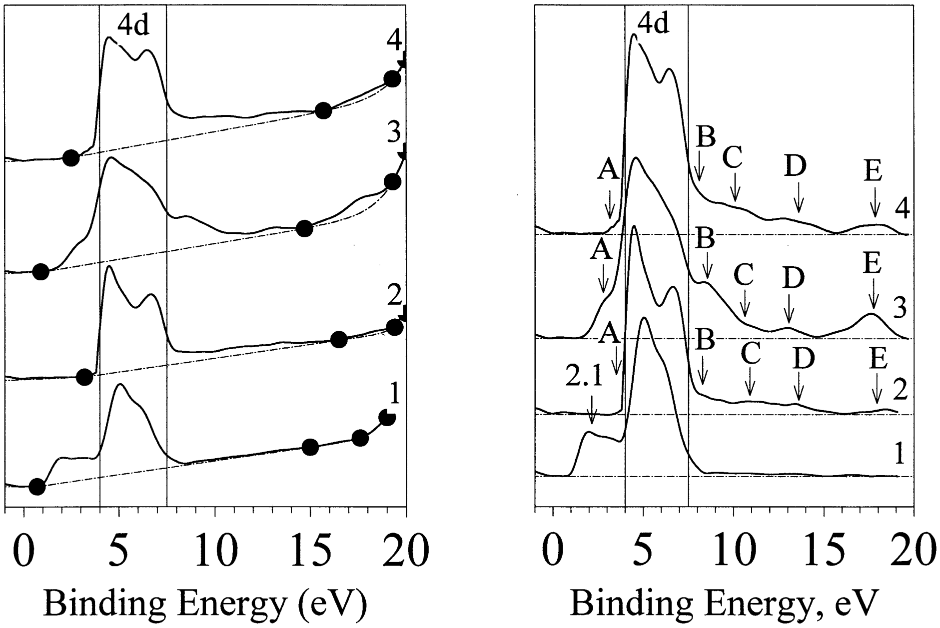

Figure 4. UPS He II spectra obtained for clean Ag_2O (curves 1) and annealed at 1000 K (curves 2) Ag_2O surface; (curves 3) spectra obtained after the RM action at $T = 770$ K ($P(C_2H_4)/P(O_2) = 10$, $P = 100$ Torr, 30 min), spectra were recorded at $T = 470$ K; (curves 4) spectra obtained after annealing of the surface treated with RM at $T = 770$ K in vacuum. The spectra were recorded at $T = 770$ K. (a) Spectra presented as recorded, dashed line is a background of scattered electrons in the approximation of linear-exponential function, black dots - points where a spectrum and background intensity coincide. (b) The difference spectra (integral spectra minus background).

quasimolecular oxygen, so we shall use this term hereafter) nature can be more stable than atomic ones. Since it is totally unusual, we paid attention to thermostable oxygen states obtained by the Ag_2O decomposition because, according to Hammond et al. [29], in this case it is possible to obtain such states in high concentration. (The detailed photoemission analysis of the oxygen states under thermal decomposition of Ag_2O was presented in ref. [36]). Also, taking into account the observations of thermostable oxygen states under high pressure gas mixture treatments by Ertl, Schlögl et al. [23–26] and Deng et al. [27] we used high-temperature treatments with a reaction mixture, too. O1s and He II spectra of annealed Ag_2O as well as after the reaction mixture action and subsequent annealing in vacuum to 1000 K are shown in figures 4 and 5. As we can see from figure 5 (curve 1), full Ag_2O decomposition with the following annealing at 1000 K results in the formation of residual oxygen (O_{res}) with $E_b = 532.0$ eV and a high O/Ag ratio close to 1/4. Argon bombardment of this sample with sputtering of the surface layers about 100–200 A showed practically the same intensity of the O1s peak. So, residual oxygen is located in the subsurface region and in the bulk as well. The corresponding UPS He II spectrum is shown in figures 4a and 4b (curves 2). We can see the existence of the photoemission features above background, so that four poorly resolved peaks (B, C, D, E) are visible in a wide range of $E_b = 0$–19 eV). (Peak A is not practically visible in this spectrum.) Thus, it confirms the idea proposed that residual oxygen inside the subsurface layers has a quasimolecular structure.

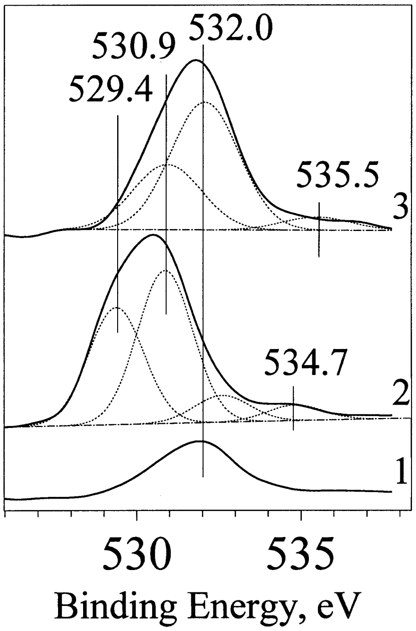

Figure 5. O1s spectra (curves 1, 2, 3) obtained under the same conditions as spectra 2, 3, 4 in figure 4. The spectra were fitted by the sum of 4 (spectrum 2) and 3 (spectrum 3) gaussians with the same full width at half maximum (FWHM), which is close to FWHM for the single oxygen states presented in figures 1 and 2.

The sample treatment with RM at $T = 770$ K results in a substantial 3.5-fold increase of the oxygen concentration so that the O/Ag ratio becomes close to 1. It is clearly seen from figure 5 (curve 2) that the increase in oxygen concentration is due to the appearance of two new oxygen states with $E_b = 529.4$ and 530.9 eV, while the initial state ($E_b = 532.0$ eV) strongly disappears. Here the most correct procedures of the spectrum deconvolution and curve fitting using the CALC program were applied. The E_b values obtained are quite close to the values reported in ref. [25], where the above main components were assigned as O_γ and O_β, respectively. Taking into account that photoemission features of O_γ (thin layer of Ag_2O) in the valence band are concentrated between 1 and 4 eV (see figure 4b (curve 1) or ref. [28]) we can reliably interpret the observed new features (figures 4a and 4b, curves 3) to be related with the oxygen state characterized by $E_b = 530.9$ eV (figure 5, curve 2). As we can see, there are five new features in the range of 4–19 eV. Thus, we can again speak about a quasimolecular nature of the oxygen state with $E_b = 530.9$ eV (O_β). A comparison of spectra 2 and 3 in figure 4 shows the redistribution of quasimolecular photoemission characteristics indicating that these oxygen states can be different species.

Annealing of the sample in vacuum after the RM treatment (figure 5, curve 3) leads to complete disappearance of the O_γ state, noticeable decrease of the O_β state as well as to the growth in the residual oxygen concentration. He II spectra again demonstrate a strong redistribution in the full valence band range, so that spectrum 4 becomes similar to spectrum 2 in figure 4. But it has more pronounced quasimolecular features due to the increase in the concentration of the residual oxygen ($E_b = 532.0$ eV). Besides, the feature A in spectrum 4 becomes clearly visible.

Wide XPS spectra show no contaminations (carbon, nickel, alkaline metals etc.) of the silver surface (and bulk as well) after annealing, so all the oxygen species discussed above can be attributed to the oxygen–silver system.

4. Discussion

Emission features of different oxygen states are compared in table 1 with data by Puglia et al. [32] and by Prince et al. [33] for gas phase and for physisorbed oxygen on Ag(110).

A usual simple approach can be used for comparison [35]:

$$E_b(\text{ads}) = E_b(\text{gas}) - \Delta\Phi - \Delta E_{\text{rel}} - \Delta E_{\text{chem}} ,$$

$$E_b(\text{ads}) = E_b(\text{phys}) - \Delta E_{\text{chem}} ,$$

Table 1
UPS characteristics of oxygen states on silver

Orbital	Oxygen states						
	O_2(gas) [32]	O_2(phys) [33]	O_{epox} E_b(O1s) = 530.5 eV	O_β E_b(O1s) = 530.9 eV	O_{res} E_b(O1s) = 532.0 eV	O_{at} E_b(O1s) = 528.2 eV	Ag_2O E_b(O1s) = 529.0 eV
2p (atomic)	–	–	–	–	–	2.5	2.1
$1\pi_g$	6.2	6.2	3.4	3.5	4–6	–	–
$1\pi_u$	10.6	10.7	7.9	8.5	8.0	–	–
$3\sigma_g$	12.2	12.0	9.6	11.2	11.1	–	–
$3\sigma_g$	14.2	14.3	12.9	13.2	13.3	–	–
$2\sigma_u$	18.5	18.6	–	17.6	18.0	–	–

where E_b(gas), E_b(phys), E_b(ads) are binding energies of the electron on the oxygen orbitals in the gas phase, physisorbed state and adsorbed state, respectively; $\Delta\Phi$ is a work function; ΔE_{rel} is an energy of the extraatomic relaxation due to transition from the gas phase to the condensed state; ΔE_{chem} is a binding energy shift due to the redistribution of the electron density upon the chemical bond formation.

For comparison, gas phase orbitals in table 1 were referenced to $1\pi_g$ of physisorbed oxygen with $E_b = 6.2$ eV. The comparison shows that the observed emission features of oxygen adsorbed states with $E_b = 530.5$, 530.9 and 532.0 eV can be reasonably related with corresponding O_2 molecular orbitals. Note that more than three additional peaks attributed to oxygen are observed in all the cases. Three oxygen features can be definitely assigned to a singlet O_2 state as discussed by Spitzer and Luth [34]. Therefore, the observed oxygen states can be characterized as a triplet adsorbed molecule. As shown by comparative calculations, the preferable triplet state of the adsorption complex can be realized due to the trapping of O_2 species inside fairly symmetrical positions in the bulk. Model cluster DFT calculations have shown the possibility of O_2 stabilization in the bulk silver octahedral position as a quasimolecular form with O–O distance ≈ 1.4 Å [37].

According to the literature data, peroxide species are more stable than superoxide ones, but peroxide species cannot produce more than three features in UPS spectra due to full spin coupling. So, the data presented here cannot be described in the frame of the two species discussed. Most probably, abnormal temperature behavior of the quasimolecular oxygen is determined by an unusual electron structure and bonding in the O/Ag system.

The observation of molecular oxygen states at high temperatures was reported before in work by Deng et al. [27]. They observed two molecular oxygen species $O_{\alpha1}$ and $O_{\alpha2}$ stable up to $T = 870$ and 770 K, respectively, on the surface of electrolytic silver. The authors gave an interpretation of these oxygen species as weakly bonded states which can appear in SERS in situ spectra on the surface in the oxygen flow due to a high gas pressure ($P(O_2) = 150$ Torr). Using data by Grant and Lambert [8] and Bao et al. [13] they related peroxide $O_{\alpha1}$ species with the α-form of molecular oxygen revealed in the papers mentioned above. For electrolytic silver, Deng et al. [13] give the desorption energy of α-form $E_{des} = 101$ kJ/mol and $\nu = 4 \times 10^{11}$ s^{-1}. Taking these data into account, let us estimate the coverage of molecular oxygen under Deng's experimental conditions ($T = 873$ K, 150 Torr O_2), using a simple approach of the adsorption–desorption equilibrium (first-order kinetics of desorption, no dependence of the adsorption rate on the oxygen coverage $(1-\theta)$):

$$[O_2] = SPF/K_{des} = S \times 1.5 \times 10^2 \times 3.6 \times 10^{20} / 4 \times 10^{11} \times 10^{-101/2.3\times8.31\times0.873} = S \times 1.7 \times 10^{16}\ \mathrm{mol/cm^2},$$

where $[O_2]$ is the oxygen concentration (mol/cm^2); S is a sticking coefficient; P the oxygen pressure (Torr); F the flow of oxygen molecules at 1 Torr per 1 cm^2 in 1 s; $F = 3.5 \times 10^{22}/\sqrt{MT}$ (M is the molecular weight of O_2; T is the gas temperature), $K_{des} = \nu e^{-E_a/RT}$ is the desorption constant.

As one can see, the sticking coefficient increase should be up to 10^{-2}–10^{-1} in order to achieve the oxygen coverage visible in SERS spectra. This value is too high for the oxygen–silver system. Typical values of the sticking coefficient are 10^{-5}–10^{-8}. Moreover, from the paper by Bao et al. [13], it follows that high enough coverage of the α-O_2 species on electrolytic silver was obtained at exposures of 10^7–10^9 L only. It gives a direct evidence of a low sticking coefficient of oxygen on electrolytic silver for the α-O_2 species (10^{-6}–10^{-8}). Thus, the proposal by Deng et al. to explain the observation of high-temperature molecular oxygen states as a shift of the adsorption–desorption equilibrium of the α-O_2 species due to the increase of the gas pressure is not likely to be reliable. Returning to the UPS results presented in this paper, we would propose that $O_{\alpha1}$ and $O_{\alpha2}$ species are most probably strongly (not weakly) bounded quasimolecular oxygen states on silver.

Finally, we would like to discuss the interpretation of the O_β-species ($\nu = 808$ cm^{-1} in SERS [27]) as an atomic one, which is also questionable. The frequency shift of 808 cm^{-1} is within typical O–O bond vibrations of 600–1100 cm^{-1}. So, it is more reasonable to attribute this state to a quasimolecular species of subsurface oxygen on silver. Our experimental XPS and UPS results indicate the molecularity of the oxygen states with $E_b = 530.5$–532.0 eV which can be very thermostable. Therefore, a speculative argument that molecular oxygen states cannot exist at high temperature contradicts with the SERS and UPS results.

But, what are the reasons for molecular oxygen to be thermostable? The theoretical work on this subject is in progress now and will be published elsewhere [37]. At this moment, we can make some speculative proposals. First, the subsurface location adds the lattice energy to the total adsorption energy (E_{ads}) of oxygen. Second, O–O bonding also gives an additional contribution to E_{ads}. Third, taking into account that thermostable O_2 states can be formed upon the strong oxygen treatment and saturation of the subsurface and bulk region with oxygen, probably an equilibrium exists between molecular subsurface oxygen O_{2ss} and atomic dissolved oxygen O_{diss}, as proposed by Ertl, Schlögl and coworkers [23–26] for O_β and O_γ species. Obviously, thermostable species cannot be formed on the surface of single crystals or on well ordered clean surfaces. As shown in ref. [25] high-temperature treatment of silver in oxygen stimulates strong restructuring of the regular surface giving rise to high extent of the surface defectiveness and thermostable oxygen states. The same point of view is reported in ref. [27] to explain the observation of thermostable oxygen states on the surface of a highly defective electrolytic silver. So, we think that two factors can be crucial for the formation of molecular thermostable oxygen states: (a) a high extent of silver saturation with oxygen and (b) a restructured surface and subsurface region.

5. Conclusions

Thus, the following conclusions can be made:

(1) The adsorbed oxygen states on silver surface with low values of $E_b(O1s) = 528$–530 eV are rather atomic species – O_{at} and Ag_2O.

(2) The oxygen states with high $E_b(O1s) = 530.5$–532.0 eV – O_{epox}, O_β, O_{res} – can be reliably attributed to different adsorbed species of quasimolecular oxygen. These states are characterized by an unusually high thermostability ($T > 800$ K) and a subsurface location.

Acknowledgement

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