Quasimolecular stable forms of oxygen on silver surface. Theoretical analysis by the density functional theory method

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Abstract

A quantum chemical investigation of possible associative oxygen forms on defective silver surface has been performed with the use of gradient-corrected density functional theory (DFT) in the cluster approximation. A surface defect was simulated by a cation vacancy (V). Cluster models (M1: Ag12 and M2: O3Ag12) of an active adsorption site (AS) with a vacancy were chosen on the basis of the structure of high-temperature layered silver oxide. The adsorbed layer on the defective surface was simulated by three oxygen atoms. For the atomic and associative (molecular) forms, the computations gave two stable structures of the adsorbed layer with C_{3V} and C_{2V} symmetry. The quasimolecular C_{2V} structure $-Ag-O-O_{ep}-O-Ag-$ resembling metal ozonides is by 44 kcal/mol more stable than the atomic C_{3V} structure. The C_{2V} structure is singlet and has an electrophilic epoxidizing oxygen atom O_{ep}. A theoretical estimation of the density of states (DOS) in the quasimolecular oxygen form revealed a complex structure below the 4d band. Additional DOS peaks in this region are due to associative O–O bonds. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Quantum chemical calculations; DFT; Silver; Dissociative and associative oxygen forms; Quasimolecular ozone-like oxygen species; Ethylene epoxidation

1. Introduction

Selective ethylene oxidation to ethylene oxide on silver was discovered by Lefort in 1933 [1]. Since that time, silver has been the only industrial catalyst used for ethylene epoxidation. This reaction takes place on some other metals, e.g., Au, Pt, Pd, Ni, Cu, but the activity of silver is higher by several orders of magnitude. Therefore, its mechanism on silver catalysts is of great importance not only for this particular reaction.

The majority of researchers believe that the unique properties of silver must be explained by the existence of different forms of adsorbed oxygen on its surface [2–6]. Dissociative (atomic) forms of adsorbed oxygen exist on all transition metals, while silver is the only metal where molecular form of oxygen also exists in noticeable concentrations at elevated temperatures.

The first systematic investigations of the mechanism of the ethylene epoxidation on silver
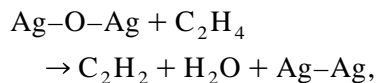
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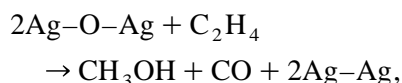*E-mail address:* via@catalysis.nsk.su (V.I. Avdeev).

were discussed, mostly, in the frames of the alternative — which form of oxygen (atomic or molecular) is active in this reaction. Early kinetic studies led to the conclusion that the atomic form was more active in this reaction [7]. However, later, it was noticed that atomic forms were more preferable for deep oxidation [2,3], while molecular forms probably accounted for partial oxidation. The best-justified molecular concept with the participation of peroxide forms Ag–O–O–Ag was suggested by Zimakov [8]. Accordingly, ethylene epoxidation involves several interconnected stages, while ethylene oxide is formed only on the surface sites with peroxide forms of oxygen:
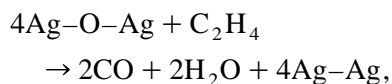
$$Ag–O–O–Ag + C_2H_4$$
$$\rightarrow C_2H_4O + Ag–O–Ag.$$
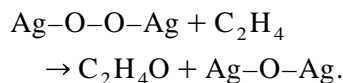
Atomic forms Ag–O–Ag are eliminated from the surface to form partial oxidation products with their subsequent transformation to CO, CO_2 and H_2O. Voge and Adams [2] complemented Zimakov's scheme. They showed that the selectivity to ethylene oxide (S) could be equal to 1/2, 2/3, 4/5 or 6/7 depending on the final products:
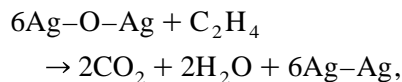
$$Ag–O–Ag + C_2H_4$$
$$\rightarrow C_2H_2 + H_2O + Ag–Ag,$$
$$S = 1/2$$
$$2Ag–O–Ag + C_2H_4$$
$$\rightarrow CH_3OH + CO + 2Ag–Ag,$$
$$S = 2/3$$
$$4Ag–O–Ag + C_2H_4$$
$$\rightarrow 2CO + 2H_2O + 4Ag–Ag,$$
$$S = 4/5$$
$$6Ag–O–Ag + C_2H_4$$
$$\rightarrow 2CO_2 + 2H_2O + 6Ag–Ag,$$
$$S = 6/7.$$

The hypothesis of the role of peroxide forms as oxygen forms active in the ethylene epoxidation was proven by Gerej et al. [9]. They analyzed the IR spectra of ethylene adsorbed on

silver at 95°C after preliminary adsorption of oxygen at 90°C, 200°C and 300°C and discriminated the adsorption band at about 870 cm^{-1} attributable to the peroxide form of oxygen. The temperature increase resulted in a change of its intensity and decrease of its frequency to 860 cm^{-1}. This led the authors to the conclusion that the peroxide forms accounted for the ethylene oxide formation, whereas the atomic species led to the formation of CO_2 and H_2O. Indeed, Vol and Shishakov [10] identified the formation of peroxide Ag–O_2 during the interaction of oxygen with silver films supported on glass with the use of electron diffraction. Thus, the molecular concept appeared to receive serious experimental proof.

However, some of the later data obtained by kinetic, adsorption, isotope and some other physicochemical methods summarized by Sachtler [11] seem to support the atomic concept of the ethylene epoxidation. Sachtler did not exclude the presence of molecular oxygen forms on the silver surface but noted that their concentration under reaction conditions cannot be high enough. It is this fact that appears to make the participation of molecular forms in the reaction very unlikely. According to van Santen and Kuipers [4] and Madix and Roberts [5], new data on the oxygen adsorption on single crystals and powders exclude the molecular concept completely.

One of the most important arguments in favor of the atomic concept is the observation of the selectivity above, $S = 6/7$, by several researchers. Analyzing the effect of modifiers and promoters, such as alkaline metals and chlorine, on the activity and selectivity of silver catalysts, van Santen and Kuipers [4] suggested a scheme presuming that the deep and partial oxidation of ethylene involve two different forms of atomic oxygen. The first atomic form with electrophilic oxygen is, presumably, a weakly bonded one-site form. It is this form that is active in the epoxidation reaction:

$$Ag = O^{\delta+} + C_2H_4 \rightarrow C_2H_4O$$
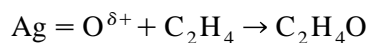
The other strongly bonded form with nucleophilic oxygen is active in deep oxidation of ethylene:

$$6Ag–O^{\delta-}–Ag + C_2H_4 \rightarrow 2CO_2 + 2H_2O$$
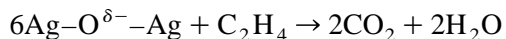
If the strongly bonded bridge form $Ag–O^{\delta-}–Ag$ can be attributed to the atomic oxygen form O_{at} [5,6,11] observed at 300 K < T < 600 K, then, what is the nature of the $Ag{=}O^{\delta+}$ form? No atomic form of oxygen on the silver surface known so far can be identified as $Ag{=}O^{\delta+}$. Furthermore, as a weakly bonded form, it can hardly exist at temperatures of real catalysis exceeding 600 K. To prove the participation of an atomic form of oxygen in the epoxidation reaction, Grant et al. [12] applied N_2O as an oxidizing agent and showed the reaction with its participation to have very high selectivity to ethylene oxide. These experiments made the majority of researchers agree with the atomic concept [5,13].

At high temperatures (T > 600 K), oxygen forms O_{ss} localized in the subsurface layers appear [14–16]. This oxygen was found to be more stable than Ag_2O oxide (cuprite) and desorbs at T > 780 K. It does not participate in the epoxidation reaction directly but is involved into exchange with oxygen in the O_{at} form.

The ethylene epoxidation reaction requires oxygen forms with electrophilic properties. Among the forms discussed above, only molecular forms have such properties. However, these forms are stabilized on regular silver surfaces only at low temperatures (T < 400 K), while the epoxidation reaction takes place at higher temperatures (T > 550 K). Not only molecular forms of oxygen, but also the atomic form O_{at} are completely desorbed at such temperatures. Meanwhile, O_{ss} is blocked and does not participate in the reaction directly. The problem is that none of these oxygen forms is active in the partial oxidation of ethylene. An ''activation'' of such surface is required. For example, for Ag(111), such activation includes prolonged exposure to the flow of oxygen and ethylene at

T = 425 K and high pressure P = 10 Torr [17]. It is commonly believed that such treatment results in the formation of subsurface oxygen O_{ss}. The latter withdraws a significant part of the electron density from the silver surface to modify the Ag–O bond and gives oxygen electrophilic properties.

In later studies, it was found that a significant reconstruction of the surface is highly probable during such treatment, which yields thermally stable oxygen with T_d > 800 K together with O_{ss} on defective surfaces [18–23]. Several values of the bonding energy of 1s-electron of oxygen in the range $E(O1s)$ = 529.0–533.0 eV were also found by X-ray photoelectron spectroscopy (XPS) for the forms with T_d > 800 K. Thus, the possible set of oxygen forms on silver is much wider. Besides the above three oxygen forms, a number of thermally stable forms, including the epoxidizing form of oxygen (O_{ep}), should be considered. It was found that O_{ep} corresponds to $E(O1s)$ = ~ 530.5 eV [19] and that it is significantly different from a more thermally stable atomic form O_γ ($E_b(O1s)$ = 529.0 eV, T_d > 900 K) observed by German researchers on a reconstructed silver surface [22]. It was proposed that O_{ep} is a quasimolecular species on the silver surface. Thus, the reconstruction of the silver surface under severe conditions involving its interaction with oxygen or the reaction mixture results in the increase of the thermal stability of both molecular and atomic forms. In other words, the molecular concept gains momentum due to the necessity in the consideration of the oxygen adsorption layer on reconstructed defective surface. So, as noted by Ponec and Bond [6], the problem has returned to square one.

The investigation of the nature of the oxygen adsorption forms on silver was a subject of a number of theoretical studies [24–33] mostly performed in the cluster approximation. Rosch and Menzel [24] conducted simulation of the atomic oxygen adsorption on silver for an Ag4–O system by the SCF-X_α method and showed that one should expect the appearance of two additional emission peaks below the Fermi level

near the 4d band of silver. Hartree–Fock (HF) calculations and qualitative analysis of the density of states (DOS) for a moderate-size cluster Ag26–O confirmed the two-peak ultraviolet photoelectron spectra (UPS) structure [25]. The results obtained by these authors, together with those reported in Ref. [28], have shown the importance of the electron correlation energy for correct estimation of the oxygen adsorption energy on silver. The HF approximation yields the bonding energy value $E(Ag–O) = 9$ kcal/mol [25], which is significantly below the experimental value (80 kcal/mol).

Selmani et al. [26] performed the analysis of the molecular adsorption of oxygen on Ag4, Ag10 and Ag16 clusters simulating the Ag(110) face by the SCF-X$_\alpha$ method. The computations of a number of oxygen adsorption states were performed for three possible orientations of the O_2 molecule with respect to the surface. A comparison of the calculated energies of one-electron levels with the XPS and UPS spectra led the authors to the conclusion that the bridge adsorption of O_2 molecules oriented parallel to the Ag(110) surface was most probable. The computations also showed DOS to have a complex structure below the 4d band, which is typical only for molecular oxygen species.

The extremely important role of subsurface oxygen forms in the formation of epoxidizing oxygen has already been mentioned. However, the mechanism of its effect is still unknown. Some aspects of this problem have been studied by the SCF-X$_\alpha$ method for a set of clusters, Ag4, Ag10 and Ag24, simulating the Ag(110) surface [29]. In particular, it was shown that the subsurface oxygen, first, weakened the Ag–O bond on the surface, and, second, increased the ethylene adsorption energy [29]. Higher adsorption energy is known to favor the epoxidation reaction and, on the contrary, hinder the combustion.

A very important attempt to determine the properties of epoxidizing oxygen was undertaken in Ref. [31]. Both the chemisorption of O and O_2, and epoxidation of olefins were ana-

lyzed by the GVB-CI method on the Ag(111) surface simulated by an Ag3 cluster. The authors [31] noted that one of the states of adsorbed oxygen $^2\Sigma$ (surface atomic oxyradical anion) was the most preferable form for epoxidation. This form of oxygen was the most electrophilic (it had the lowest effective charge, $q(O) = -0.20$). The role of electronegative promoters was also studied in this paper and was interpreted in a manner slightly different from the one suggested by other authors [27,29].

Jorgensen and Hoffmann [32] studied general aspects of the atomic and molecular adsorption of oxygen on silver by the extended Huckel method and suggested several models for the oxygen insertion into the π-bond of ethylene. The atomic form of oxygen was preferred for epoxidation. It was also noted that DOS of molecular forms had at least two peaks below the 4d band, which is in a qualitative agreement with the results in Ref. [26]. In a series of theoretical studies by Nakatsuji summarized in review [33], main intermediates in the ethylene epoxidation reaction with participation of atomic and molecular forms of oxygen were calculated with the use of the dipped adcluster model (DAM). Their calculations predict that adsorbed molecular superoxide is the oxygen form active in this reaction.

So, which form of oxygen — molecular or atomic — is active in the epoxidation of ethylene? Neither experimental, nor theoretical results were able to solve this problem unambiguously. However, it should be noted that only oxygen forms on regular surfaces were discussed in the cited theoretical papers. We believe that the ''activation'' of oxygen results in a dramatic change of the adsorption layer due to the reconstruction of the surface. New quasi-molecular forms of oxygen can be formed on such surface. Their properties are very different from those of the low-temperature molecular forms mentioned above. No well-reasoned molecular model of oxygen forms on the surface or in the subsurface layers of silver metal has been suggested so far.

In the present paper, a model of an active site (AS) of the Ag–O–V–O–Ag type with a cation vacancy V is suggested and theoretically justified. At high temperatures, the vacancy captures a surface O_s or subsurface O_{ss} oxygen atom to form a quasimolecular structure with electrophilic epoxidizing oxygen Ag–O–O_{ep}–O–Ag. The suggested concept of electrophilic oxygen active in the ethylene epoxidation on silver makes it possible to explain all available experimental data consistently from common positions.

2. Theoretical results

2.1. Cluster models of oxygen adsorption on defective surface

The structure of the surface with strongly bonded forms of oxygen is unknown. As such structure is formed at high pressures and temperatures when the oxygen dissolution in the bulk is significant [14], it is necessary to begin with determining the properties of O_{ss} oxygen. Subsurface oxygen structures are usually described in terms of Ag_2O oxide. In other words, they are assumed to have the Ag_2O lattice, in which oxygen is atomic. However, as shown by the theoretical analysis [34], associative forms of oxygen can also be formed in the bulk during the relaxation of the lattice, which can be as high as 8% of the lattice parameter [35]. A model of semi-rigid crystal, where only relaxation of the first coordination sphere including the oxygen molecule is allowed, was used in Ref. [34]. Fig. 1 presents the simplest cluster Ag14 consisting of two spheres. The first coordination sphere, which consists of six silver atoms marked in Fig. 1, has the distorted octahedron symmetry. In this case, associative oxygen forms with $R(O–O) = 1.401$ Å along the C_4 axis and $R(O–O) = 1.436$ Å along the C_3 axis are formed.
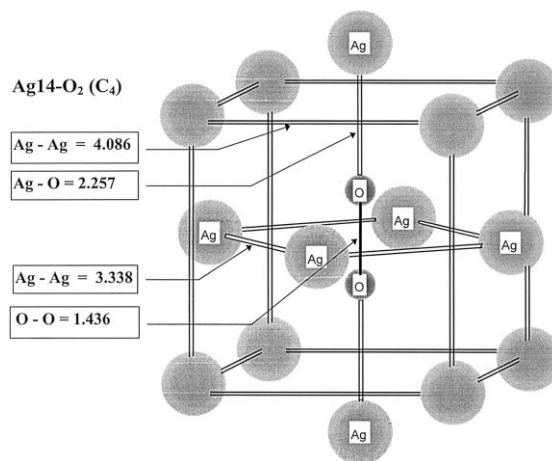

Fig. 1. Cluster model Ag14–O_2 of dissolved oxygen. The O_2 molecule is placed into the octahedral hole along a C_4. The relaxation of silver atoms of the first coordination sphere was taken into account in the computations. The second coordination sphere (eight external silver atoms) was fixed at $R(Ag–Ag) = 4.086$ Å.

However, the estimated heat of reaction Ag14 + 2O → Ag14–O_2 does not exceed $\Delta H = -94$ kcal/mol [34]. As this value is lower than the energy of the O–O bond in the gas phase $E(O–O) = 118$ kcal/mol, associative forms in the bulk are thermodynamically unstable. The surface reconstruction results in the formation of various defects favoring the segregation of oxygen. For example, several variants are possible for the formation of a cation vacancy on the surface (–Ag–V–Ag–). The oxygen segregation on the surface leads to its transformation into a more stable dissociative form –Ag–O–V–O–Ag– with the following oxygen desorption. However, further stabilization of the adsorbed layer is possible if the vacancy captures atomic oxygen to form an associative form –Ag–O–O–O–Ag–. Which of these variants is actually realized? To answer this question, it is necessary to construct an AS model explicitly involving a surface defect.

It is reasonable to take a cation vacancy as the defect. As the ethylene epoxidation is performed at temperatures higher than the Ag_2O decomposition temperature, it was natural to construct the AS model on the basis of the other

high-temperature layered oxide with the trigonal structure P_{3ml} (D_{3d}) [36]. The structural motive of this oxide is presented in Fig. 2. If one forms a cation vacancy V in the first silver layer on the axial axis and cuts hemispheres with $R = V - r_j$, a number of clusters will be obtained. Two such clusters M1: Ag12 and M2: O3Ag12 are shown in Fig. 2. In such oxide, two silver layers are separated by an oxygen layer with bond lengths $R(Ag1–O) = 2.161$ Å and $R(Ag1–Ag1) = 3.072$ Å in one layer and $R(Ag1–Ag2) = 3.041$ Å between the layers. The distance between the silver layers is $h = 2.471$ Å.

Based on this oxide, Bao et al. [22,23] described one of the thermally stable forms of oxygen with the desorption temperature above 900 K and $E_b(O1s) = \sim 529.0$ eV. They inter-

preted this form as surface-embedded oxygen O_γ. In contrast to Ref. [22,23], our model of AS includes a cation vacancy as an important element. As it will be shown below, the behavior of oxygen near a vacancy is significantly different from that on a regular surface.

Model M1 consists of two silver layers with the hexagonal structure simulating defective metal surface, whereas model M2 simulates defective metal surface with subsurface oxygen O_{ss}. As follows from the data obtained by scanning tunneling microscopy (STM) and reflection electron microscopy (REM) [22,23,37,38], similar structures are indeed formed during the treatment of the surface under severe conditions ($T > 800$ K and high partial oxygen pressure). It has been noted that complete reconstruction of the Ag(111) surface takes place under such conditions. It results in the formation of a hexagonal configuration of silver atoms with deep holes filled with oxygen in the center of each hexagon.

We believe that the formation of vacancies is determined by the diffusion of silver and oxygen atoms not only due to high temperature, but also due to the additional effect of modifiers (carbon, chlorine, cesium, oxygen) and local overheating during the energy dissipation caused by the action of the reaction medium. Under conditions of the catalytic reaction, the above factors are realized simultaneously and favor a significant decrease of the surface reconstruction temperature with the fixation of the vacancies by oxygen in the form of its thermally stable species.

2.2. Computational methods

Most of the results were obtained in the frames of the density functional theory (DFT) [39]. The widespread application of this method to the computation of the electronic structure of molecules started when effective algorithms for calculation of the exchange correlation energy E_{xc} in the Kohn–Sham equation exceeding the
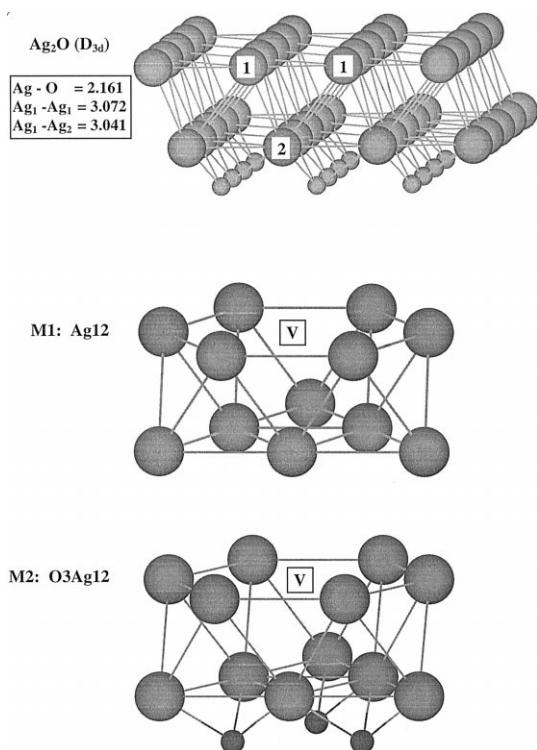

Fig. 2. Structure of layered silver oxide Ag$_2$O (D_{3d}) and cluster models (M1 and M2) of oxygen AS constructed on its basis. Cluster M1 simulates AS of a clean metal surface with a cation vacancy *V*. Cluster M2 simulates AS with subsurface oxygen. Structural parameters of M1 and M2 were fixed in the calculations at the values typical for regular Ag$_2$O (D_{3d}).

traditional local density approximation (LDA) were suggested [40]. These approximations consist in the account of gradient corrections from the electron density to the exchange (E_x) and correlation (E_c) energy in expansion (1):

$$E_{xc} = \sum_i A_i \left[E_x^i + E_c^i \right] \qquad (1)$$

The LDA approximation with the Slater exchange local functional E_x^{SLT} [39] and Vosko–Wilk–Nusair correlation functional E_c^{VWN} [41] is taken as the first component of this row. In the three-parameter method B3LYP suggested by Becke [42], certain parts ($\sim 20\%$) of the exchange energy are preserved in ''pure'' HF form E_x^{HF}, while gradient corrections to the exchange energy are saved out as a separate component (B88 functional). The correlation component is exchanged for the Lee–Yang–Parr (LYP) functional [43] with a minor admixture of E_c^{VWN}. In this variant, there are only three parameters in Eq. (1):

$$E_{xc} = A E_x^{SLT} + (1 - A) E_x^{HF} + B E_x^{B88} + C E_c^{LYP}$$
$$+ (1 - C) E_c^{VWN} \qquad (2)$$

Parameters A, B and C are usually determined empirically. In Ref. [44], these parameters were determined via a linear mean-square interpolation of the atomization energies and ionization potentials for a set of molecules containing atoms of the first three periods. The following optimal values were obtained: $A = 0.80$, $B = 0.72$, and $C = 0.81$. This approximation was used in the present study.

The calculations were performed with the use of a program set GAUSSIAN92/DFT [45]. Core electrons of silver ($1s^2 \ldots 3d^{10}4p^64s^2$) were included into the effective potential with the corresponding LANL1DZ basis for valence ($4d^{10}5s^1$) electrons and LANL2DZ basis for valence ($4p^64s^24d^{10}5s^1$) electrons [46]. O(9s5p) + G**(6-31G**) $\rightarrow$ O[4s2p2d] [47] with exponents for polarization d-functions $\alpha = 1.6$ and 0.4 was used for description of the associative and dissociative adsorption forms for a group
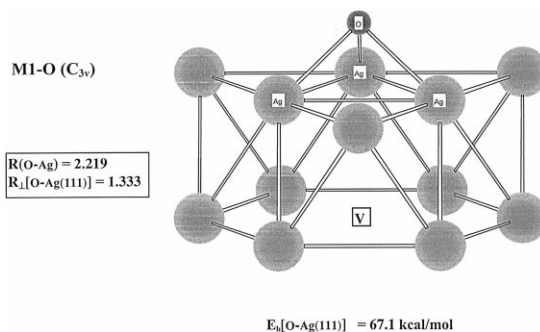

M1-O (C_{3v})

R(O-Ag) = 2.219
$R_\perp$[O-Ag(111)] = 1.333

E_b[O-Ag(111)] = 67.1 kcal/mol

Fig. 3. Atomic three-fold adsorption of oxygen on Ag(111) in two-layer model M1. Trigonal C_3 axis passes through oxygen and cation vacancy V.

consisting of three oxygen atoms. The 3-21G basis was used for the subsurface group also consisting of three oxygen atoms O_{ss}.

The B3LYP/LANL2DZ/6-31G** approximation satisfactorily describes energies of O–O, Ag–Ag and O–Ag bonds. For Ag_2 and O_2 molecules, the calculations give bond energies $E_b(Ag–Ag) = 35.8$ kcal/mol and $E_b(O–O) = 122$ kcal/mol. The experimental values are $E_{exp}(Ag–Ag) = 38.3$ kcal/mol and $E_{exp}(O–O) = 118$ kcal/mol [48]. However, B3LYP with the accepted basis underestimates the bond energy $E_b(O–Ag)$. In the B3LYP/LANL1DZ/6-31G** approximation, the oxygen bond energy on regular Ag(111) surface for model M1 (Fig. 3) E_b[O–Ag(111)] = 67.1 kcal/mol is 9.5 kcal/mol below the experimental value E_{exp}[O–Ag(111)] = 76.6 kcal/mol [49]. That is why significant underestimation of the oxygen and ozone adsorption energies on silver are possible in the calculations. Therefore, we operated only with relative stability of the associative and dissociative oxygen forms during the theoretical analysis of the structure of the oxygen adsorption layer. A qualitative estimation of the thermodynamics of the ozone formation on silver was performed by the MP4SDTQ/LANL2DZ/6-31G** method for the simplest reaction:

$$3/2 O_2 + Ag_2 \rightarrow O_2 + O + Ag_2 \rightarrow O_3 + Ag_2$$
$$\rightarrow Ag_2\text{–}O_3. \qquad (I)$$
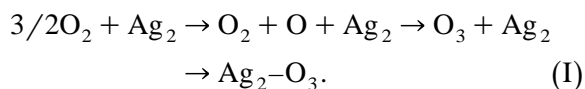
In this case, a more consistent account of the electron correlation energy gives approximately the same precision for the energy of all reaction components.

2.3. Structure of the adsorption layer on defective silver surface

At high coverage, the structure of adsorbed oxygen on the surface resembles that of a bulk oxygen layer in silver oxide [36] shown in Fig. 2. For the models M1 and M2 used, the adsorption layer consists of three oxygen atoms. As has already been noted, the formation of a cation vacancy is highly probable at high temperatures due to removing silver atoms from the surface. The presence of a vacancy destroys the stability of the adsorption layer. Therefore, it seemed very important to find new configurations of the layer structure stabilized by oxygen. So, an optimization of oxygen atoms adsorbed near the vacancy was performed. All structural parameters of clusters M1 and M2 were fixed at the values of layered Ag_2O, and only the positions of the oxygen atoms with respect to the surface were optimized.

The results of the calculation of two stable structures with the symmetry of the adsorbed state C_{2V} and C_{3V} for cluster M2 are presented in Fig. 4. As it could be expected, the atomic adsorption layer with the C_{3V} structure practically copies the structure of the regular oxygen layer O_{ss}. The presence of the vacancy modifies three-fold bonds of oxygen with the surface to two-fold classic $Ag–O_{at}–Ag$ bonds for Ag (I). Bond lengths $R(Ag–O_{at})$ decrease slightly, and interatomic distances $R(O_{at}–O_{at})$ increase from 3.07 to 4.11 Å. Strong polarization of oxygen (effective Mulliken charge $q(O_{at}) = -0.65$) and bond length $R(Ag–O) = 2.08$ Å typical for oxides (Fig. 4) characterize an ionic $Ag^+–O^{2-}$ bond with nucleophilic oxygen.

The other structure C_{2V} is significantly different from C_{3V} because the configuration of the adsorption layer is changed due to the asso-
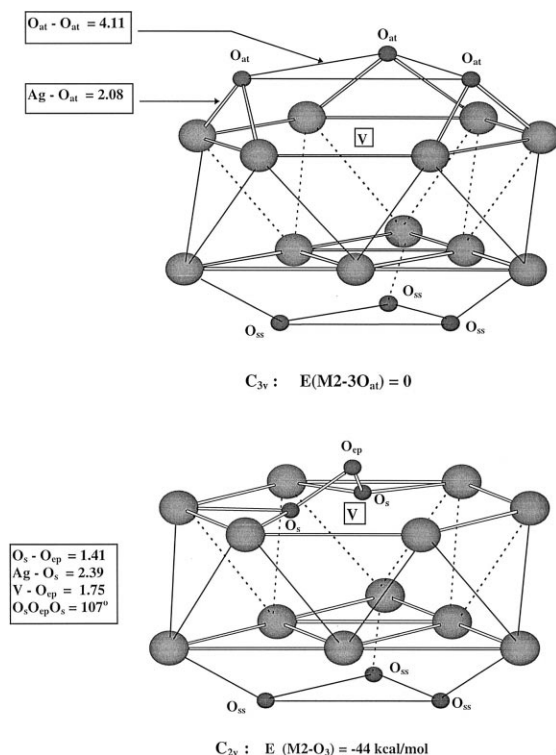

Fig. 4. Structure of dissociative (C_{3V}) and associative (C_{2V}) oxygen forms on the silver surface with a cation vacancy V for model M2. Total energy $E(C_{3V})$ of complex M2–3O_{at} was taken as the zero point. Stabilization of the associative form relative to the dissociative one $\Delta E = E(C_{3V}) - E(C_{2V}) = 44$ kcal/mol.

ciation of three oxygen atoms. The two-center bridge bond of one oxygen atom with silver ($Ag–O–Ag$) is substituted by a two-center bond with oxygen ($O–O–O$). Such structural rearrangement is possible only due to the cation vacancy. As it will be shown below, the central atom of such structure has electrophilic properties and is denoted as O_{ep} in Fig. 4.

The following restrictions were imposed during the optimization of this structure: O_{ep} oxygen had only one degree of freedom along the trigonal axis of cluster M2 with fixed dihedral angle $\angle O_s(V–O_{ep})O_s = 120°$. With these restrictions, the calculation gave $R(O_s–O_{ep}) = 1.41$ Å and $\angle(O_s–O_{ep}–O_s) = 107°$. In comparison with the atomic structure $Ag–O–Ag$, the bond length $Ag–O_s$ increased in this molecular structure $Ag–O_s–O_{ep}–O_s–Ag$, the charge of terminal

oxygen atoms decreased to $q(O_s) = -0.35$, and the charge of the central oxygen atom decreased almost to zero. Altogether, this structure is less polarized with more covalent Ag–O bonds and markedly expressed electrophilic properties of the central oxygen atom.

However, the most remarkable feature of the C_{2V} structure is its significantly higher stability in comparison with that of the C_{3V} structure. With the total energy taken as the zero point $E(C_{3V}) = 0$, the calculations yield the stabilization energy $\Delta E(C_{2V}) = 44$ kcal/mol. The literature lacks reports about molecular forms of oxygen on the surface that would be more stable than atomic ones. The experimental values of the adsorption energy of molecular oxygen do not exceed $\Delta H_{ad} \sim 10$–13 kcal/mol [49] on regular Ag(110) and Ag(111) surfaces and $\Delta H_{a\pi c} \sim 25$ kcal/mol on defective surfaces, such as electrolytic silver [50]. In contrast to conventional peroxide (O_2^{2-}) and superoxide (O_2^{1-}) forms, the suggested associated form consists of three oxygen atoms. The structure and properties of the C_{2V} oxygen form are close to those of an ozone molecule bonded with silver atoms via terminal O_s atoms [1]. This adsorbed C_{2V} structure will be hereafter called quasimolecular ozonide-like structure.

There are some parallels between the C_{2V} structure and that of silver ozonide AgO_3 formed in matrix-isolated reactions $Ag + O_3$ in argon [51]. In Ref. [51], it was concluded that the bands observed in the region of 800 cm^{-1} were due to the vibrations of the O–O bond in AgO_3. The formation of physisorbed O_3 on Ag(111) leads to the shift of the frequency to $\nu_{as} = 1030$ cm^{-1} [52]. The corresponding frequency in the

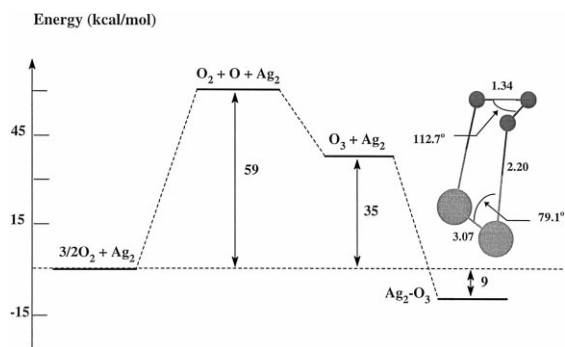Fig. 5. Thermodynamics of the formation of a quasimolecular ozone-like form of oxygen on silver exemplified for the simplest system $Ag_2 + O_3$.

gas phase is $\nu_{as} = 1042$ cm^{-1} [53,54]. So, large frequency shift is caused by the formation of the one-fold Ag–O$_3$ chemical bond. The M2–O$_3$ complex exhibits significantly higher stability than silver ozonide AgO_3. Such complex can be formed only at high temperatures when the surface reconstruction with the following substitution of silver atoms for oxygen atoms is possible. In this case, stronger multicenter bonds Ag–O–O–O–Ag are generated on silver surface. It is possible to show a basic opportunity of formation of similar bonds on the example of reaction (I). For a sufficient, full account of the electron correlation energy, the calculation of all reaction products was performed in the MP4SDTQ approximation [45] (with the geometry optimization by the B3LYP/LANL2DZ method with fixed bond length $R(Ag-Ag) = 3.07$ Å). Its results are presented in Fig. 5. The heat of reaction $O_2 + O \rightarrow O_3$ in the gas phase is $\Delta H = -24.6$ kcal/mol [55,56]. This energy is not sufficient for compensation of one half of the O–O bond cleavage energy (59 kcal/mol). An ozone molecule will be stabilized on a surface only if its adsorption energy is not less than 35 kcal/mol. Calculations (excluding zero-point vibrational energy corrections) give $\Delta H_{ad}(O_3) = -44$ kcal/mol. This estimation shows the possibility of the formation of quasimolecular ozone-like oxygen forms on silver.

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[1] The following values were obtained for the ground singlet state of ozone O_3 by the B3LYP method with the O(9s5p)+G** $\rightarrow$ O[4s2p2d] basis and C_{2V} symmetry: bond length $R(O-O) = 1.262$ (1.271) Å, angle $\angle(O-O-O) = 118°$ (117°), dipole moment $\mu = 0.58$ (0.53) D, heat of reaction $O_2 + O \rightarrow O_3$, $\Delta H = -17$ (-24.6) kcal/mol. The experimental values are given in parentheses.

2.4. DOS of adsorbed oxygen for models M1 and M2

DOS is a fundamental characteristic of photoelectron emission spectra. In contrast to solid-state methods (band structure calculations), the energy spectrum in cluster calculations is discrete due to a finite size of the cluster. A simple method is being used for qualitative analysis of DOS in the cluster approximation. A Gauss or Lorentz distribution is defined for each individual level. Then, the summation of the local distributions is performed with given line half-width taking into account of the occupation of one-electron levels. We used the Lorentz distribution:

$$f(\varepsilon) = (2/\pi\gamma)\left[1 + \varepsilon^2/\gamma^2\right]^{-1} \qquad (3)$$

Fig. 6 presents DOS obtained by the Lorentz broadening of the discrete energy spectrum with the parameter $\gamma = 0.5$ eV for clusters M1 and M2. The Fermi level was taken as the zero
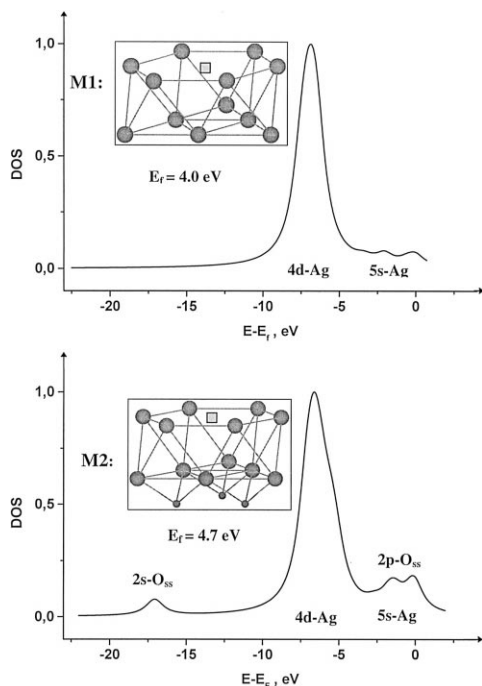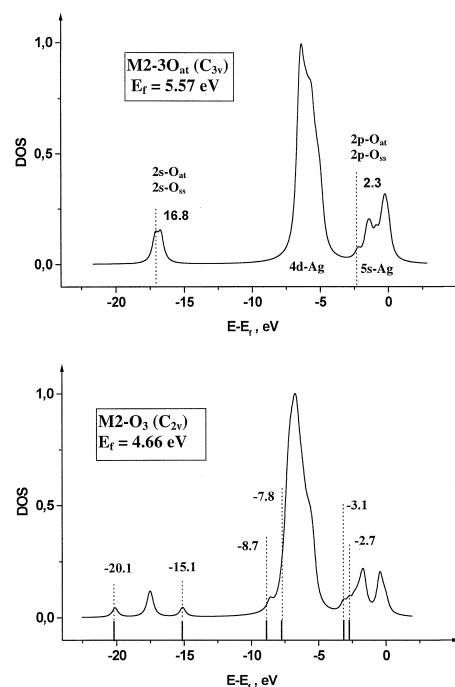

Fig. 7. DOS valence band for atomic M2–3O(C_{3V}) and quasi-molecular M2–O$_3$(C_{2V}) adsorption layers (see text for details).

Fig. 6. DOS of the valence band for models M1 and M2. ($\square$) denotes a cation vacancy (see text for details).

point. Theoretical values of the Fermi levels were determined from the position of the highest occupied energy level. In this approximation, $E_F = 4.0$ eV for M1. This value can be compared with the work function for different silver surfaces $\varphi = 4.1$–4.75 eV [57]. The increase of the Fermi energy for M2 ($E_F = 4.7$ eV) is due to the presence of the subsurface oxygen. Comparing the spectra of M1 and M2, it is possible to see that the subsurface oxygen modifies DOS structure near the Fermi level due to the overlapping of the 5s band of silver with the 2p oxygen level. Furthermore, an additional 2s oxygen level appears below the intensive 4d band.

The formation of a cation vacancy does not have a significant effect on the integral DOS. However, as mentioned above, it radically changes local properties of the adsorption site. DOS for two structures of the adsorption layer C_{3V} and C_{2V} discussed above are shown in Fig. 7. In the case of the atomic adsorption form

M2–3O_{at} with the C_{3V} structure, the intensity in the range $E - E_F = -1.5 \div -2.55$ eV increases, and an additional peak resulting from the interaction of the oxygen 2p atomic orbitals with the 5s and 5p orbitals of silver appears at 2.3 eV. The Fermi level increases further to $E_F = 5.57$ eV. However, DOS does not exhibit any structure different from that of free metal surface below the 4d band up to the 2s level of oxygen.

The situation is significantly different for the C_{2V} structure. The $C_{3V} \rightarrow C_{2V}$ transition corresponds to the formation of quasimolecular oxygen in our model. First, this effect results in the decrease of the Fermi energy by $\Delta E_F \sim 1$ eV in comparison with the atomic adsorption. It is caused by a sharp decrease of the effective charge on oxygen atoms in the ozonide structure due to the formation of the electrophilic oxygen O_{ep} (see Fig. 4). However, the most important effect is the appearance of an additional DOS structure below the 4d band at $E - E_F = -20.1$, -15.1, -8.7, and -7.8 eV, and above the 4d band at $E - E_F = -3.1$ and -2.7 eV. The last two adjacent levels are similar to those observed for the atomic form at 2.3 eV, being shifted to higher bond energies by the interaction of $2p\pi$ electrons of oxygen in the ozonide structure. It also causes the splitting of the 2s band of oxygen into two components -20.1 and -15.1 eV. Finally, the levels at -8.7 and -7.8 eV are due to the interaction of the $2p\sigma$ electrons of oxygen with the 4d electrons of silver. Thus, the difference of associative forms of oxygen from dissociative ones consists of the appearance of additional peaks below the 4d band.

3. Discussion

It was found earlier that the oxygen treatment of Ag(111) at $T > 670$ K results in the appearance of a number of oxygen states including O_{ep} state with $E_b(O1s) = 530.4$ eV [21]. The analysis showed that it is more likely for this form to have molecular properties rather than atomic

ones [19,20]. In this form, oxygen does not possess high polarizing ability. Its effective charge is not very high as the change of the work function connected with the formation of this form is much smaller than in the case of O_{at}. Besides, the Ag3d spectra do not exhibit ionic components during the adsorption of this type of oxygen. This form has been shown to account for the ethylene epoxidation, its desorption temperature exceeding 800 K [58]. It is noteworthy that $E_b(O1s)$ values in oxides Ag_2O_2, Ag_2O (cuprite), Ag_2O (O_γ) and atomic form O_{at} on the surface do not exceed 529.0 eV. This value is significantly smaller than $E_b(O1s)$ = 530.4 eV observed for O_{ep}. Moreover, the latter value is typical for various molecular forms on the surfaces [59].

The O_{ep} state exhibits a complex UPS. For Ag(111) additional peaks are formed below the 4d band with the binding energies $E_b = 7.3$, 9.4, 12.3 and 16.9 eV [21]. Such UPS structure cannot be explained by the dissociative oxygen adsorption. However, such spectrum finds a natural explanation in the frames of the associative concept. The calculations show that the multiple structure below the 4d band results from the stabilization of quasimolecular ozone-like forms of oxygen on the silver surface with a cation vacancy. Without any doubt, the peak $E_b = 16.9$ eV is due to the 2s electrons of oxygen.

It has been mentioned above that the formation of associative forms of oxygen results in the splitting of the 2s level into two components with $\Delta E = 5$ eV (Fig. 7). The experimental peaks at $E_b = 16.9$ and 12.3 eV can be correlated with the theoretical values of the two components of the 2s level with $E_b = 20.1$ and 15.1 eV, while the experimental peaks at $E_b = 9.4$ and 7.3 eV correspond to the theoretical values 8.7 and 7.8 eV, respectively. There is an uncertainty in the origin of peak $E_b = 7.3$ eV located at the edge of the 4d band. Still, the calculations show that, although the level -7.8 eV is ''shadowed'' by the intensive 4d band (Fig. 7), the corresponding peak is undoubtedly related to oxygen. Thus, the complex UPS struc-

ture below the 4d band cannot be attributed to an atomic form and should be identified in accordance with the theoretical results as a quasimolecular form with epoxidizing oxygen O_{ep}.

According to our concept, the quasimolecular oxygen species are formed from adsorbed or subsurface atoms rather than by direct molecular oxygen adsorption from the gas phase. The stabilization mechanism is related to the fact that the Ag–O bond energy decreases with the growth of the O/Ag ratio at high surface coverages with oxygen. Under certain conditions, the formation of the surface complex [–O–Ag–O–Ag–O–] becomes less energetically favorable than that of the surface complex [–Ag–O–O–O–Ag–]. Silver has the lowest Me–O bond energy among transition metals [60]. This fact might account for its uniqueness as a catalyst for this reaction. Other metals have significantly stronger Me–O bonds making the formation of quasimolecular oxygen via this mechanism require more severe conditions or completely impossible.

The suggested AS concept makes it possible to present the general epoxidation mechanism as a series of stages without their detailed consideration. At high temperatures, equilibrium between surface and subsurface forms of oxygen, including dissolved oxygen, is established:

$$O_2 + -Ag-Ag-Ag-$$
$$\Leftrightarrow -O_s-Ag-Ag-Ag-O_s-$$
$$\Leftrightarrow -Ag-O_{ss}-Ag-O_{ss}-Ag- \qquad (II)$$
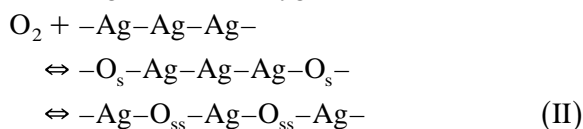
Stage (II) indicates that active oxygen species are formed from *atomic oxygen* irrespective of its origin and molecularity. High oxygen pressure facilitates the reconstruction of the surface with the formation of the cation vacancies. As noted above, the surface reconstruction results in the formation of the hole hexagons. Though they may be thermodynamically unstable themselves, they can be stabilized by oxygen in a quasimolecular form due to the fast oxygen exchange on the surface and in the bulk ($O_s \Leftrightarrow O_{ss}$).
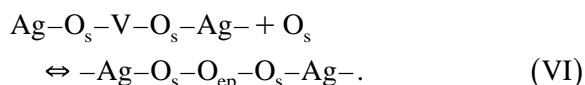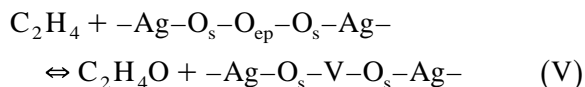
One can suppose that a great variety of other structural forms and defects are formed during the surface reconstruction but they are subsequently annealed to the initial forms because of the lack of their stabilization by oxygen. These complex processes are schematically summarized by stages (III) and (IV):

$$-Ag-O_{ss}-Ag-O_{ss}-Ag-$$
$$\Leftrightarrow -Ag-O_s-V-O_s-Ag-Ag- \qquad (III)$$
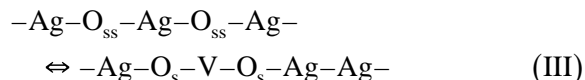
Stage (IV) reflects high mobility of oxygen in the bulk and on the silver surface during the formation of the high-temperature quasimolecular layer. As shown above, this stable structure includes electrophilic oxygen O_{ep}:

$$O_s + -Ag-O_s-V-O_s-Ag-$$
$$\Leftrightarrow -Ag-O_s-O_{ep}-O_s-Ag- \qquad (IV)$$
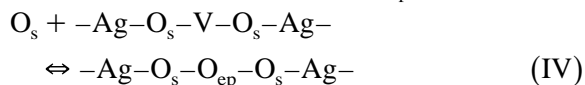
The following stages include the epoxidation reaction itself (V) and the AS regeneration (VI):

$$C_2H_4 + -Ag-O_s-O_{ep}-O_s-Ag-$$
$$\Leftrightarrow C_2H_4O + -Ag-O_s-V-O_s-Ag- \qquad (V)$$
$$Ag-O_s-V-O_s-Ag- + O_s$$
$$\Leftrightarrow -Ag-O_s-O_{ep}-O_s-Ag-. \qquad (VI)$$

Summary equation of stages II, III, IV, V, VI can be written as follows:

$$C_2H_4 + 2O_2/Ag \longrightarrow C_2H_4O + \left[\begin{array}{c} Ag-O \\ Ag-O \end{array} \!\!\!\! O \right]$$
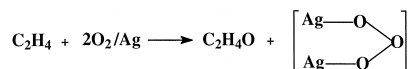
Let us discuss some consequences of the suggested epoxidation scheme with participation of quasimolecular oxygen (called hereafter ''ozonide'' scheme). First, this mechanism does not have limitations for the maximum selectivity $S = 6/7$ appropriate for earlier molecular schemes. It can be easily noted that one O_2 molecule forms two AS, yielding two ethylene oxide molecules via stages (IV), (V) and (VI). Therefore, in this scheme the selectivity to ethylene oxide can be as high as 100%. Besides, the ozone-like form is thermally stable providing high steady-state coverages under catalytic conditions.

The known problem of molecular mechanism related with the isotope mixing in the adsorption layer [3,4] is also solved in the frames of this epoxidation mechanism model. Stage (IV) presumes that atomic and molecular forms of oxygen are in equilibrium. At low coverages, the equilibrium is shifted to the left (atomic forms), while at high coverages it is shifted to the right, and associative forms predominate. As a dissociative form of oxygen always precedes the formation of associative ones, the composition of the reaction products must correspond to the full mixing case. This corresponds to the model of an energetically uniform adsorption layer for the isotope exchange $^{16}O_2 + {}^{18}O_2 \rightarrow 2\,{}^{16}O^{18}O$ suggested by Boreskov et al. [61]. Therefore, such isotope experiments cannot be a criterion distinguishing between the atomic and molecular reaction mechanisms, and oxygen forms cannot be differentiated into atomic and molecular ones by their isotope mixing. The ozone-like adsorption layer can behave as a uniform layer in the kinetic aspect, although it is not structurally uniform. Then, it is necessary to note that this approach harmonizes to some extent the contradictions in the results obtained by kinetic [62] and spectral methods that reveal several states of oxygen on the surface.

Experiments performed by Grant et al. [12], who have shown that the use of N_2O instead of molecular oxygen in the feed results both in the deep and selective oxidation, are also not unambiguous. Assuming that the decomposition of nitrous oxide results in the stabilization of oxygen only in the atomic form, they considered that this fact is decisive for the description of the epoxidation reaction in the frames of the atomic concept. As noted above, the source of atomic oxygen is not important for the formation of associative oxygen forms on the silver surface, as electrophilic oxygen is formed at the final stage after the association of oxygen atoms into an ozonide structure.

Using theoretical conceptions on associative mechanisms in catalysis developed by Boreskov [63], we would like to draw attention to the possibility of a concerted epoxidation mechanism, which assumes coupling of the ethylene interaction with the regeneration of the ozonide structure (stages V and VI in the above scheme). This concerted mechanism can provide high selectivity of the process. In the case of the consecutive epoxidation and ozonide regeneration reactions, there is a possibility of the destruction of the reduced AS structure ($Ag–O_s–V–O_s–Ag$) with the annealing of the vacancy and transformation of oxygen into the atomic state active in deep oxidation. Naturally, this process can decrease the selectivity of the ethylene oxidation.

4. Conclusion

The calculations of the adsorption layer consisting of three oxygen atoms on defective silver surface have shown that associative (quasimolecular) forms of oxygen are stabilized by the cation vacancies, and predominate over dissociative forms at high coverages. A model of an ozone-like AS with electrophilic oxygen O_{ep} has been suggested. The analysis of the valence electron energies for the O_{ep} form has been performed, and the calculated DOS structure has been shown to be in a qualitative agreement with the experimental UPS data.

It has been shown that the structure of peaks induced in the valence band by the epoxidizing oxygen O_{ep} is multiplicative due to the association of O–O bonds in the form of a quasimolecular ozone-like structure. These results have been used as a basis of suggested general mechanism for the ethylene epoxidation, which can eliminate the main contradictions between ''atomic'' and ''molecular'' concepts known in the literature.

Acknowledgements

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