

VI RUSSIAN CONFERENCE
ON CATALYTIC REACTION MECHANISMS
(Moscow, October 1–5, 2002)

Surface State of a Silver Catalyst for Ethylene Glycol Oxidation

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Received November 5, 2002

Abstract—The surface state of electrolytic silver before and after treatment with a reaction mixture in the course of ethylene glycol oxidation to glyoxal was studied using X-ray photoelectron spectroscopy and scanning electron microscopy. It was found that electrophilic forms of adsorbed oxygen, which participate in the selective conversion of ethylene glycol, were formed on the surface of electrolytic silver crystals under exposure to oxygen under conditions similar to catalytic process conditions. The treatment of the catalyst with a reaction mixture resulted in the formation of filamentous carbon deposition products. A mechanism of formation of carbon-containing products was proposed.

INTRODUCTION

Silver is a unique catalyst for a number of industrial processes of oxidative organic synthesis: ethylene oxidation to ethylene oxide, methanol oxidation to formaldehyde, ethylene glycol oxidation to glyoxal, etc. However, even the mechanisms of well-studied processes such as ethylene oxidation [1, 2] and methanol oxidation [3, 4] cannot be considered conclusively established, although they have been intensely discussed in the literature for a long time. The greatest difficulties in studying important aspects of these mechanisms are due to the limitations of the physicochemical techniques in use, which cannot be implemented at actual process temperatures and pressures of reaction mixture components. Thus, in studies of the surface state of silver treated with oxygen, which were performed to determine the structure of active centers, the fact that carbon was actively inserted into the structure of commercial silver catalysts under real conditions was ignored. However, it cannot be doubted that carbon considerably affects surface properties [5]. The use of catalysts in the form of single crystals or foil also results in the disappearance of the effects of specific structural features of a real catalytic system, the treatment of the catalyst with a reaction mixture, the diffusion of mixture components through defects in the bulk of the catalyst, etc. [6]. Thus, in spite of experimental difficulties, the mechanistic studies of reactions under real conditions are undoubtedly of scientific and practical interest.

In this study, we were the first to compare the surface states of a bulk silver catalyst before and after treatment with a reaction mixture under conditions as close to real process conditions as possible. This study was performed in order to detail the mechanism of partial oxidation of ethylene glycol to glyoxal.

EXPERIMENTAL

The test samples were filamentary crystals of silver prepared by the electrolysis of an AgNO_3 melt in a rotating cathode electrolysis bath ($T = 543\text{--}560\text{ K}$, 32–34 wt % AgNO_3 in a $\text{KNO}_3\text{--NaNO}_3$ melt) at the Institute of High-Temperature Electrochemistry, Ural Division, Russian Academy of Sciences [7]. The fine cleaning of sample surfaces was performed according to the procedure described in detail elsewhere [8].

The silver samples were treated with a reaction mixture containing ethylene glycol, O_2 , N_2 , and H_2O in a catalytic flow unit at a 2-cm height of the catalyst bed. The reaction mixture was introduced at the top end of the reactor. After the treatment of the catalyst with the reaction mixture, the sample was cooled in a flow of nitrogen. The reaction products were analyzed by chromatography [9].

X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical composition of sample surfaces. The photoelectron spectra of silver catalyst samples were obtained with the use of a VG ESCALAB spectrometer. The procedure of spectroscopic measurements for studying silver catalysts was detailed elsewhere [10–12].

The samples were fixed on a holder with a conducting vacuum-stable double-sided adhesive tape in air. Before spectroscopic measurements, the samples were evacuated in a pretreatment chamber to the residual gas pressure $P = 10^{-5}\text{ Pa}$; thereafter, they were transferred to an analyzer chamber in which the base vacuum was at a level of 10^{-7} Pa . The main background gases were CO , CO_2 , and H_2O .

Spectroscopic information was processed using standard graphical packages and the CALC program. To quantitatively evaluate the chemical composition,

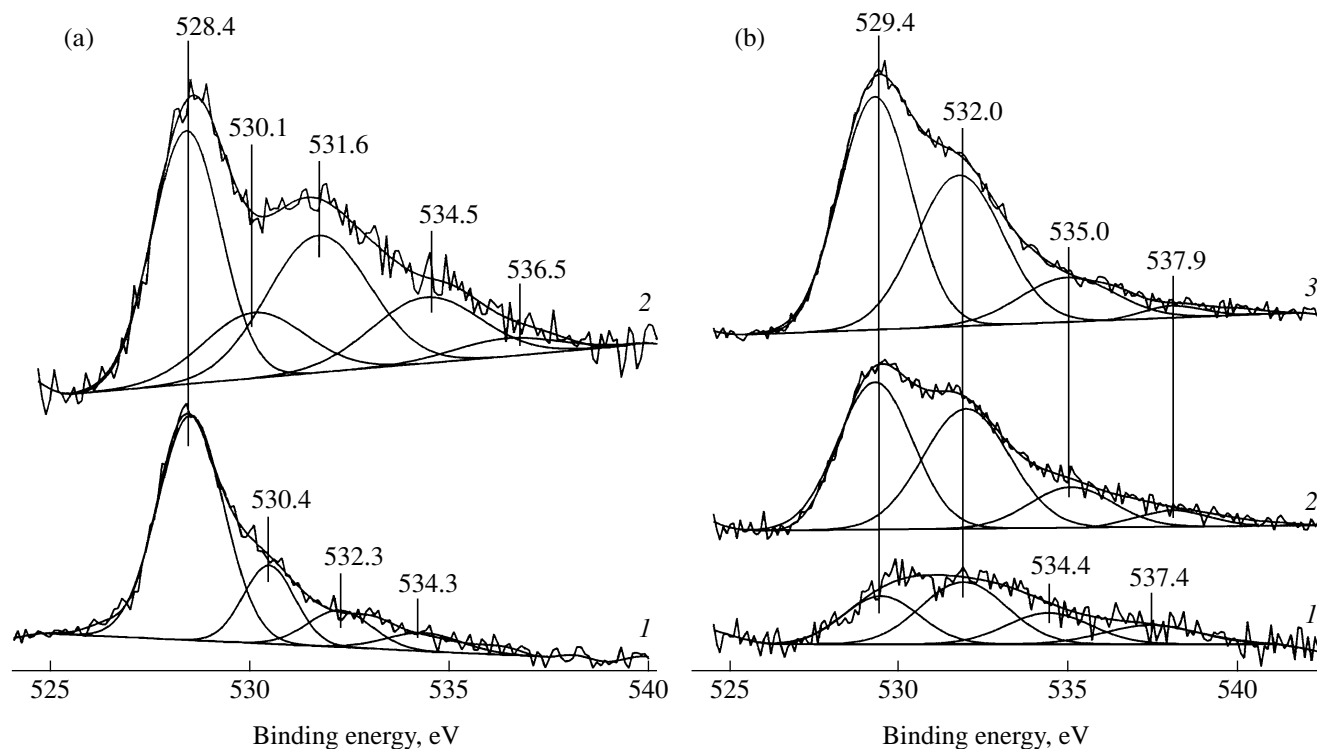


Fig. 1. XPS O1s spectra of silver samples treated with oxygen under various conditions: (a) (1) silver (110) single crystal ($T = 473$ K; $P = 1$ Pa) and (2) electrolytic silver ($P = 500$ Pa; $T = 473$ K); (b) annealing of the electrolytic silver sample (pretreated with O_2 at $T = 473$ K and $P_{O_2} = 1000$ Pa for 30 min) (1) at 723 K; after the treatment of electrolytic silver with oxygen ($P = 1000$ Pa; $T = (2) 723$ or (3) 773 K).

the most intense lines of the elements were precisely recorded. The concentration ratio between particular components in a sample was determined from the integrated line intensities of corresponding atomic levels with consideration for tabulated empirical atomic sensitivity factors [13].

The surface morphology was studied with the use of a BS 350 Tesla scanning electron microscope. To improve topographic contrast, a gold film 100 Å in thickness was supported on the surface of the samples.

RESULTS AND DISCUSSION

The states of oxygen on the (110) surface of a silver single crystal and on the surface of an electrolytic silver sample, which were treated with oxygen under identical temperature conditions, were compared using the XPS O1s spectra shown in Fig. 1a. In both samples, an oxygen species with $E_b(O1s) = 528.4$ eV was observed, which was attributed to the surface oxide Ag_2O_s [10]. This surface oxygen species is active in the deep oxidation of CO and organic compounds such as ethylene [1, 14], methanol [4], and ethylene glycol [15]. It can be seen in Fig. 1a that a line with $E_b(O1s) = 528.4$ eV was predominant for the Ag(110) single crystal (spectrum 1). At the same time, along with Ag_2O_s , oxygen-containing

centers with a greater binding energy were present in the sample of electrolytic silver; the intensity of these centers was comparable to the intensity of the oxide species (spectrum 2). The state of oxygen characterized by $E_b(O1s) = 531\text{--}537$ eV can be represented by the following species: O^- , O_2^- , O_2^{2-} , O_3^- , OH^- , O_2 , and H_2O [2, 12, 16, 17]. The interpretation of these states of oxygen on silver remains controversial. Nevertheless, because in the Ag_2O_s oxide a maximum negative charge is localized on the oxygen atom, that is, this oxygen is essentially nucleophilic, the other states of oxygen with greater $E_b(O1s)$ detected on silver exhibit a knowingly lower polarity of the Ag–O bond, and these species can be classified as “electrophilic” species.

Thus, the electrophilic species of adsorbed oxygen are formed on the surface of polycrystalline electrolytic silver under exposure to O_2 ; the amount of these species is comparable to that of the oxide species. It is likely that different ratios between oxygen species on the Ag(110) single crystal surface and on the surface of electrolytic silver are a consequence of the highly defective structure of the latter.

The tendency for the surface of electrolytic silver to form electrophilic oxygen species, which are characterized by an increased strength of bonds to the catalyst

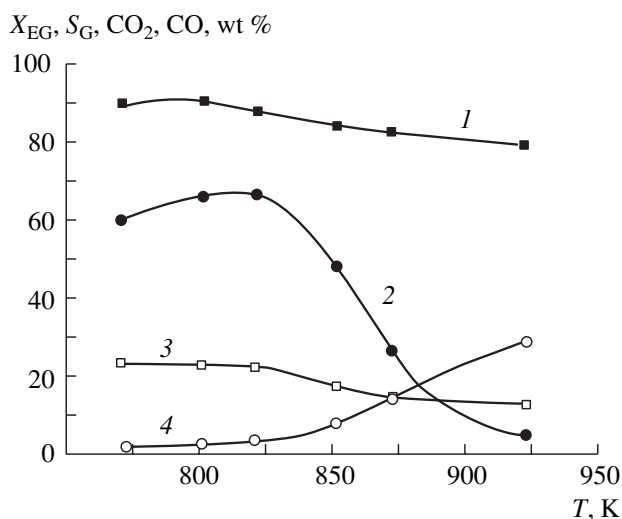


Fig. 2. Temperature effect on the oxidation of ethylene glycol to glyoxal on an electrolytic silver catalyst (O_2 /ethylene glycol/ N_2 / $H_2O = 1.1 : 1.0 : 13.0 : 5.2$): (1) ethylene glycol conversion (X_{EG}), (2) selectivity for glyoxal (S_G), (3) yield of CO_2 , and (4) yield of CO .

surface, became even more pronounced as the temperature of sample treatment with oxygen was increased (Fig. 1b). Vodyankina *et al.* [15] observed the formation of oxygen species with covalent Ag–O bonds, which were active in the partial oxidation of ethylene glycol, as the temperature of oxygen adsorption and the time of surface treatment were increased.

The surface oxide in an electrolytic silver sample pretreated with oxygen ($T = 473$ K, $P_{O_2} = 1000$ Pa; 30 min) completely decomposed in the course of annealing at $T = 723$ K (Fig. 1b, spectrum 1), as evidenced by the disappearance of the corresponding line at 528.4 eV from the $O1s$ spectrum. At the same time, only the intensity of electrophilic species decreased; this fact suggests that they are much more thermally stable than the Ag_2O_s oxide. It is most likely that the thermal stability of these species is associated with the localization of oxygen atoms at defect sites of the near-surface region of silver. A further high-temperature treatment of the electrolytic silver sample with oxygen (Fig. 1b, spectra 2, 3) increased the intensities of electrophilic species; in this case, the formation of oxide-like oxygen was not observed. The $O1s$ spectrum (Fig. 1b, spectrum 3) was taken from the silver sample under near-catalytic conditions, that is, at a high oxygen pressure (1000 Pa) and a temperature that occurs in the industrial reactors of ethylene glycol oxidation. Thus, it is believed that one or several oxygen species detected on the catalyst surface under these conditions (Fig. 1b, spectrum 3) are constituents of the active center that is responsible for the selective conversion of ethylene glycol.

Figure 2 demonstrates data on the catalytic activity of a sample of polycrystalline silver in the reaction of

ethylene glycol oxidation. These data were obtained on varying temperature, which was determined at a “hot” spot of the catalyst bed. The highest selectivity for glyoxal was reached at a temperature of 800–823 K, which is consistent with experimental data obtained by Gallezot *et al.* [18]. The glyoxal content of the reaction products decreased as the temperature was further increased. This was due to glyoxal decomposition to CO and H_2 , as evidenced by a simultaneous increase in the yield of carbon monoxide. A decrease in the conversion of ethylene glycol and in the yield of CO_2 over a temperature range of 820–923 K can be associated with silver surface restructuring under exposure to high temperature, which resulted in defect annealing, so that oxygen species responsible for deeper oxidation of the alcohol were formed on the ordered surface.

The surface morphology of the electrolytic silver sample before and after treatment with the reaction mixture was studied using scanning electron microscopy (SEM). The initial crystals were branched elongated fibers with a smooth surface (Fig. 3a). Figures 3b and 3c demonstrate the surface morphology of catalyst grains treated with the reaction mixture at $T = 823$ K for 1 h. It can be seen that the surface of silver crystals underwent considerable changes. Silver grains were coated with filamentous carbon deposition products with a whisker thickness of 0.1–0.5 μm .

Note that the distribution of carbon deposits along the catalyst bed was nonuniform. Whereas the top part of the bed (Fig. 3b) retained its initial light color, the appearance of black catalyst grains due to the accumulation of a considerable amount of carbon deposits was detected in the bottom part (Fig. 3c). The accumulation of the bulk of carbon deposits at the bottom of the catalyst bed was due to a change in the composition of the reaction mixture along the catalyst bed. The concentration of oxygen decreased and the concentration of products (primarily, glyoxal, which is the main coal-forming agent [19]) simultaneously increased in the bottom part of the reactor. Thus, favorable conditions for the buildup of carbon deposits due to glyoxal, which resulted from the reaction in the top layers of the catalyst, were produced in the bottom part of the reactor.

On the other hand, it cannot be excluded that, upon reaching a critical thickness, carbon deposits can exfoliate from the surface of silver grains in the top part of the catalyst bed, as found previously [19], and accumulate on catalyst grains in the bottom part of the reactor. In this case, new carbon-containing structures in the form of whiskers were generated on the released surface of the silver crystal; that is, the growth and exfoliation of carbon deposits is a cyclic process.

According to XPS data, the action of the reaction mixture changed the surface composition of the test sample (table). The contact of oxygen with the surface of a decarbonized electrolytic silver sample (Fig. 1a, spectrum 2) did not detectably increase the oxygen content (table). As compared with the surface composition

of the purified electrolytic silver treated with O_2 (table, sample 1), the oxygen content of the near-surface region of the catalyst considerably increased after the treatment of electrolytic silver with the reaction mixture (sample 2). This is consistent with published data [20] on an increase in the rate of oxygen insertion into the bulk of silver in the presence of impurity carbon and on an increase in its concentration.

Figure 4 demonstrates the $O1s$ and $C1s$ spectra of silver grains taken from the top and bottom layers of the catalyst. It can be seen that the chemical surface composition of catalyst samples treated with the reaction mixture is determined by the degree of accumulation of carbon-containing products. In this case, the structure and composition of oxygen species in the $O1s$ spectrum depend on the concentration of carbon deposits (Fig. 4a).

The spectra obtained from the surface of grains taken from the bottom part of the catalyst bed (sample 3; Fig. 4, curve 2) indicate that the surface concentrations of carbon and oxygen significantly increased (by a factor of ~ 10); this is associated with an increase in the amount of carbon deposits on the surface of the test sample (Fig. 3c). On the surface of sample 3 (table), oxygen almost completely constitutes carbon–oxygen structures rather than silver oxides. Thus, regardless of the history of electrolytic silver sample treatment with reaction mixtures of different compositions, a correlation between the concentrations of oxygen and carbon as catalyst surface constituents was found.

All oxygen and carbon species detected on the surface of sample 3, which was fully covered with carbon deposits, can be ascribed to carbon-containing structures because, according to quantitative estimations (table), the surface silver content of this catalyst was very low. Correspondingly, the amount of oxygen as a constituent of adsorption species directly on the silver surface was insignificant as compared with oxygen as the constituent of carbon deposits.

Taking into account the capability of ethylene glycol and glyoxal (which take part in the test reaction) to form polymeric structures, we propose the following interpretation of the $O1s$ and $C1s$ spectra: In the $C1s$ spectra of the resulting carbon deposits, the main component is a peak with $E_b(C1s) = 284.6$ eV. According to data [21], this peak corresponds to either atomic carbon or carbon clusters, including aggregated graphite-like structures. Glyoxal polymerization and/or ethylene glycol polycondensation can result in the formation of C–O–C ether bonds and C–O–H alcohol groups. The occurrence of these bonds and groups in the carbon deposits was supported by the presence of components with $E_b(O1s) = 531.1$ eV and $E_b(C1s) = 286.3$ eV [21]. Oxygen species with $E_b(O1s) = 529.8$ eV and carbon species with $E_b(C1s) = 288.2$ eV can be ascribed to $-COOH$ and $-CO_3^{2-}$ groups [10, 21], which are bound to silver atoms and/or are the constituents of carbon

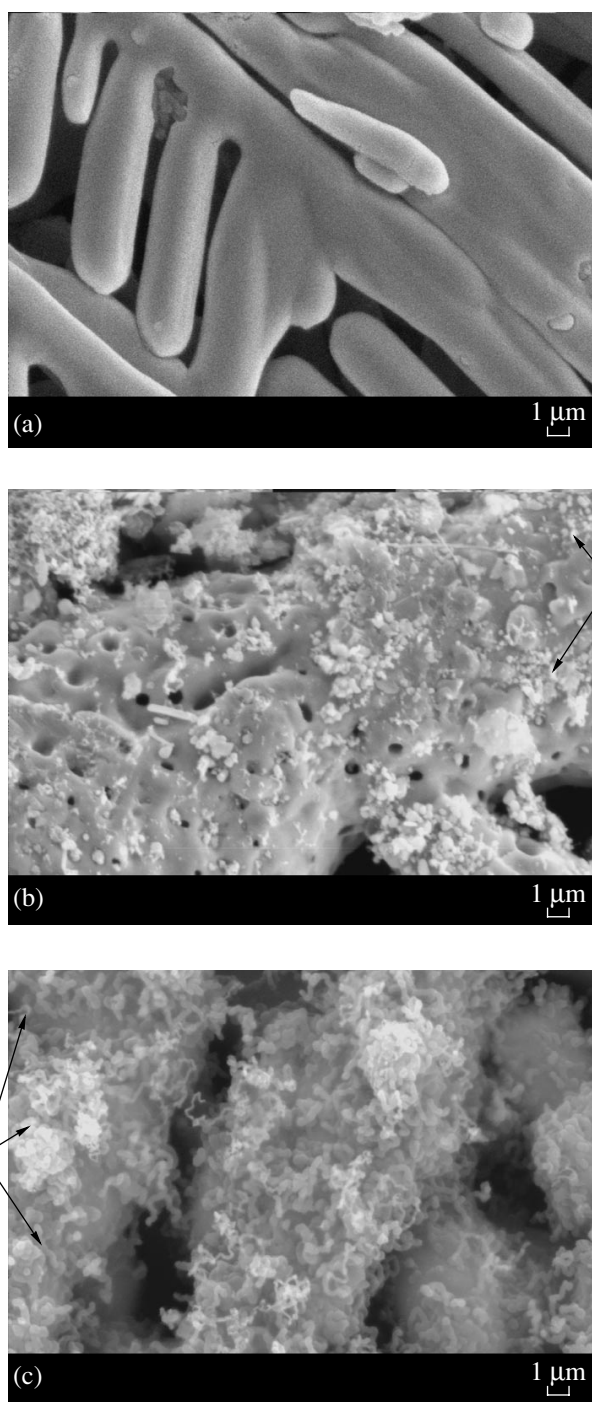


Fig. 3. Surface morphology of electrolytic silver (a) before and (b, c) after treatment with the reaction mixture O_2 /ethylene glycol/ N_2 / H_2O = 1.1 : 1.0 : 9.0 : 5.2 at $T = 823$ K for 1 h; the samples were taken from the (b) top and (c) bottom parts of the catalyst bed. Arrows indicate filamentous carbon deposits.

deposits, whose surface may be oxidized because of contact with oxygen of the reaction mixture. The component of the $O1s$ spectrum with $E_b = 533.0$ eV can be attributed to H_2O molecules incorporated into the struc-

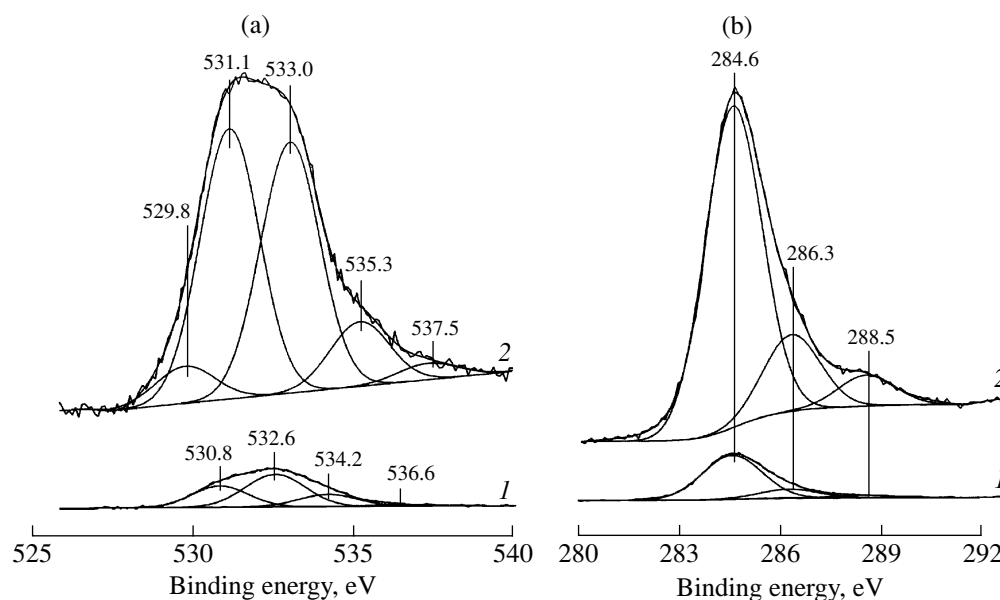


Fig. 4. XPS (a) O1s and (b) C1s spectra of silver catalysts treated with the reaction mixture $\text{N}_2/\text{O}_2/\text{ethylene glycol}/\text{H}_2\text{O} = 10.0 : 1.0 : 1.0 : 3.4$ at 823 K for 60 min; the samples were taken from the (1) top and (2) bottom parts of the catalyst bed.

ture of carbon deposits. These water molecules can result from the dehydration of polymer structures, or they can be supplied from the reaction mixture.

Note that the characters of the C1s spectra were identical for the samples taken from the opposite regions of the catalyst; that is, they are independent of the amount of carbon deposition products on the surface of silver. This suggests a single mechanism of carbon deposition on the surface of silver catalysts in the course of ethylene glycol oxidation.

A comparison of the morphology characteristics and data on the chemical composition of the surface allowed us to assume that carbon deposits formed in the course of the partial oxidation of ethylene glycol exhibit a complex structure with chemically different regions. It is likely that carbon clusters form the basis of the carbon deposits; these clusters are practically free of oxygen. Polymer structures containing C–O–C and C–O–H groups are inserted between the carbon

clusters. These structures are formed by the polycondensation of ethylene glycol or glyoxal within the pores or cavities of carbon clusters. The top layer of carbon deposits, which was continuously exposed to oxygen of the reaction mixture, consisted of carbon structures containing a maximum amount of oxygen.

It is likely that the complex multilayer system grew because of an increase in the size of carbon clusters on the insertion of reaction products into accessible cavities in carbon deposits. These products underwent polymerization and subsequent deoxygenation accompanied by the ejection of water vapor and CO_2 with the formation of new cavities. The catalyst surface may be regenerated either because of the combustion of carbon deposits or because of the exfoliation of carbon deposits as the critical thickness was achieved.

Thus, the surface of silver underwent considerable changes under exposure to the reaction mixture. These

Chemical composition of the surface of Ag catalysts treated under various conditions

Sample no.	Silver sample	C/Ag*	O/Ag	C/O
1	Electrolytic silver crystals after decarbonization followed by treatment in oxygen (1000 Pa, 773 K)	0.00	0.02	0.00
2	Top zone of the catalyst bed at 773 K for 1 h**	2.62	0.64	4.10
3	Bottom zone of the catalyst bed at 773 K for 1 h**	22.40	6.80	3.30

Notes: * The relative atomic concentrations of the elements were calculated in terms of one silver atom.

** Electrolytic silver crystals after treatment in the reaction mixture $\text{O}_2/\text{N}_2/\text{ethylene glycol}/\text{H}_2\text{O} = 1.0 : 10.0 : 1.0 : 3.4$.

changes are associated with the formation of structurally complex carbon deposits.

CONCLUSIONS

Electrophilic species of adsorbed oxygen are mainly formed on the surface of the test electrolytic silver in the reaction with oxygen. The concentration of these electrophilic species increases with the temperature of treatment. Based on a comparison of spectroscopic and catalytic data, we concluded that one or more electrophilic species on the surface enter the composition of active centers that are responsible for the selective conversion of ethylene glycol into glyoxal.

Filamentous carbon-containing products are deposited on the Ag-catalyst surface under exposure to the reaction mixture. We proposed a single mechanism for the formation of carbon deposits in the course of ethylene glycol oxidation over wide ranges of temperatures and ratios between the components of the reaction mixture. We believe that carbon deposits are formed via the polycondensation of reaction products followed by the deoxygenation of the resulting structures. We found that graphite-like clusters alternated with polymer structures with high oxygen content are the constituents of carbon deposits.

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