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Role of Phosphates in the Promotion of Silver Catalysts for Partial Oxidation: I. Structure and Properties of Phosphates on the Surface of Polycrystalline Silver

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Abstract—The chemical composition, structure, and properties of an H_3PO_4-promoted polycrystalline silver foil are studied by XPS. The surface of the doped sample contains oxygen in two states with binding energies of 531.1 and 533.0 eV. Heat treatment results in silver clusters distributed in the polyphosphate matrix. It follows from TDS data that the surface of the promoted catalyst contains a strongly bound oxygen species that desorbs at ~900 K. It is believed that the silver clusters stabilized by the phosphate matrix are active sites on the surface of the phosphorus-promoted catalyst.

INTRODUCTION

To enhance the selectivity of processes, various promoters are introduced in catalysts. Study of the physicochemical properties of doped systems is a key for the design and production of catalysts for particular purposes.

Silver is a well-known catalyst for ethylene epoxidation, the oxidation of methanol to formaldehyde and of ethylene glycol to glyoxal, and other reactions [1]. Phosphorus-containing compounds are used as promoters to enhance the selectivity of the silver catalyst for the partial oxidation of alcohols [2, 3]. The effect of these compounds on the activity of silver catalysts has been studied in detail. Much less attention has been given to the state of the catalyst surface, the nature of oxygen species, and the mechanism of catalysis by phosphorus-doped silver.

This work presents a detailed study of the interaction between phosphoric acid and the surface of bulk silver and of the properties of the resulting compounds by the XPS and TDS methods.

EXPERIMENTAL

The starting material was silver foil (99.9995%) with a thickness of 50 μm. It was placed in a VGESCALAB HP (VG Scientific, United Kingdom) electron spectrometer.

Experiments consisted of two stages. At the first stage, the chemical state of the surface of unpromoted silver foil was studied. At the second stage, a promoter was deposited onto the sample surface by treating the surface with a phosphoric acid solution (40 wt %, special purity grade) for 5 min at T = 298 K followed by drying at 473 K for 10 min. Next, the behavior of the phosphorus-containing chemical compounds on the silver surface was studied as a function of temperature.

Samples of both the starting and promoted foils were heated in the chamber of the spectrometer. The temperature was increased from 333 to 923 K in 50 K steps (the heating rate was 1 K/min). At each temperature point, the sample was held for 20 min, and then an XPS spectrum was recorded. Next, the sample was cooled from 923 to 473 K in 150 K steps (temperature-arrest time, 20 min; cooling rate, 1 K/min) and its XPS spectrum was again recorded. Oxygen was admitted to the hot sample in the preparation chamber of the spectrometer, and the chamber was pumped at a preset adsorption temperature.

The base vacuum in the chambers of the spectrometer was 10^{-8} Pa. The foil surface was cleaned in cycles including ionic etching and heating *in vacuo*. Recording XPS spectra for silver catalysts is detailed in [4–6]. Electron emission was excited by AlK_α X-ray radiation. The mean free path of electrons, λ, was 20–30 Å, depending on the spectral line. The surface was examined to a depth of the order of 3λ = 60–90 Å.

TDS experiments were performed with the use of a quadrupole mass spectrometer placed in the analytical chamber of the spectrometer. The completion of gas evolution during heating was checked by monitoring the peaks due to the formation of CO, CO_2, and H_2O. Temperature control and peak intensity recording for the vacuum-heated samples were carried out with a high degree of accuracy at a heating rate of 1 K/min using the specially created software Tandem.

The electron emission spectra were processed with the Easyplot and Origin standard graphic packages and

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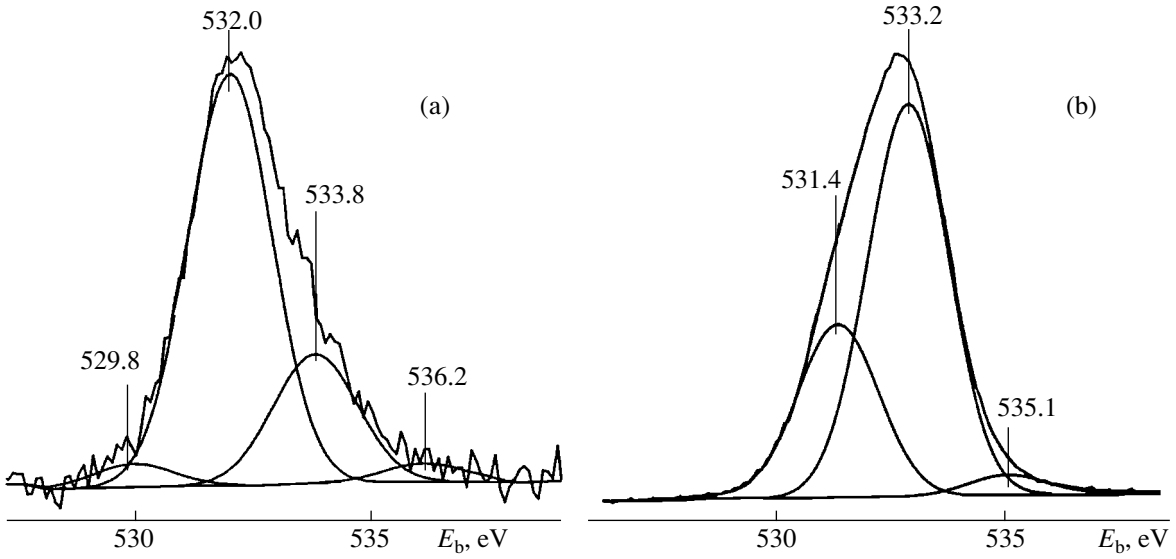


Fig. 1. O1*s* spectra of silver foil (a) before and (b) after promotion with H_3PO_4 (the samples were treated with O_2 at P_{O_2} = 500 Pa and T = 623 K for 30 min).

the specially created software WinCalc. To estimate the chemical composition, the most intense lines of elements were recorded. Component ratios in samples were determined from the corresponding integral line intensities, taking into account empirical atomic sensitivity factors [7].

RESULTS AND DISCUSSION

Figure 1 presents the O1*s* spectra from the surface of silver foil before and after treatment with phosphoric acid. The clean silver surface treated with oxygen at 500 Pa and T = 623 K is very inhomogeneous as to the state of oxygen. It is dominated by two states characterized by binding energies E_b(O1*s*) of 532.0 and 533.8 eV. These states can be assigned to "subsurface" oxygen located in subsurface defects of the silver lattice [8–11]. The peak at 529.8 eV can be assigned rather reliably to oxide oxygen [12, 13]. As to the weak peak at E_b(O1*s*) = 536.2 eV, its energy is abnormally high for any adsorbed oxygen species and it is likely to be due to water and oxygen molecules occluded in the micropores and defects of the polycrystalline sample as a result of treatment with oxygen or a reaction medium under severe conditions.

The treatment of the foil surface with phosphoric acid results in a significant change in the oxygen spectrum (Fig. 1b): all components of the oxygen species disappear and two new oxygen states with the energies 531.4 and 533.2 eV appear, which, according to [7], can be assigned to the bridging oxygen in the Ag–O–P and P–O–P groups and to the terminal oxygen in the P=O group, respectively. The E_b(O1*s*) = 535.1 eV peak becomes visible only after deconvolution of the spectrum into components and is likely to be assignable to water included in the structure of phosphoric acid on the silver surface.

Figure 2a shows the O1*s* spectra of the silver foil surface treated with H_3PO_4 and heated from 333 to 923 K (spectra *1–6*). A significant shift of the core electron lines is observed during heating. The lines shift to higher E_b as the temperature is increased to 423 K and to lower binding energies as the temperature is raised from 423 to 923 K. This effect is likely to be due to the changes in the surrounding of oxygen atoms in the phosphorus-containing layer, primarily water desorption. Characteristically, the O1*s* peaks do not shift significantly as the sample is stepwise cooled (Fig. 2b, spectra *6–9*).

Figure 3 plots the P2*p* peak position as a function of temperature. The P2*p* peak shifts in the same way as the O1*s* line in Fig. 2. This fact gives unambiguous evidence that phosphorus and oxygen are chemically bonded. The general trend is that the P2*p* peak shifts with increasing temperature to lower binding energies, suggesting that orthophosphate-to-polyphosphate conversion takes place [7], which implies water loss.

The shift of the oxygen lines to lower binding energies can also be due to the diffusion of silver atoms to the phosphorus-containing layer. The silver diffusion results in a decrease in the O : Ag atomic ratio, as can be seen in Fig. 4, while the O : P ratio does not change. The possibility of migration of silver as Ag^+ ions in the structure of complex phosphate systems, for example, ion-selective membranes, has widely been discussed [14–16]. Note that cooling the sample does not return the surface to its starting state, which is characterized by a high O : P ratio (Fig. 4, dotted line).

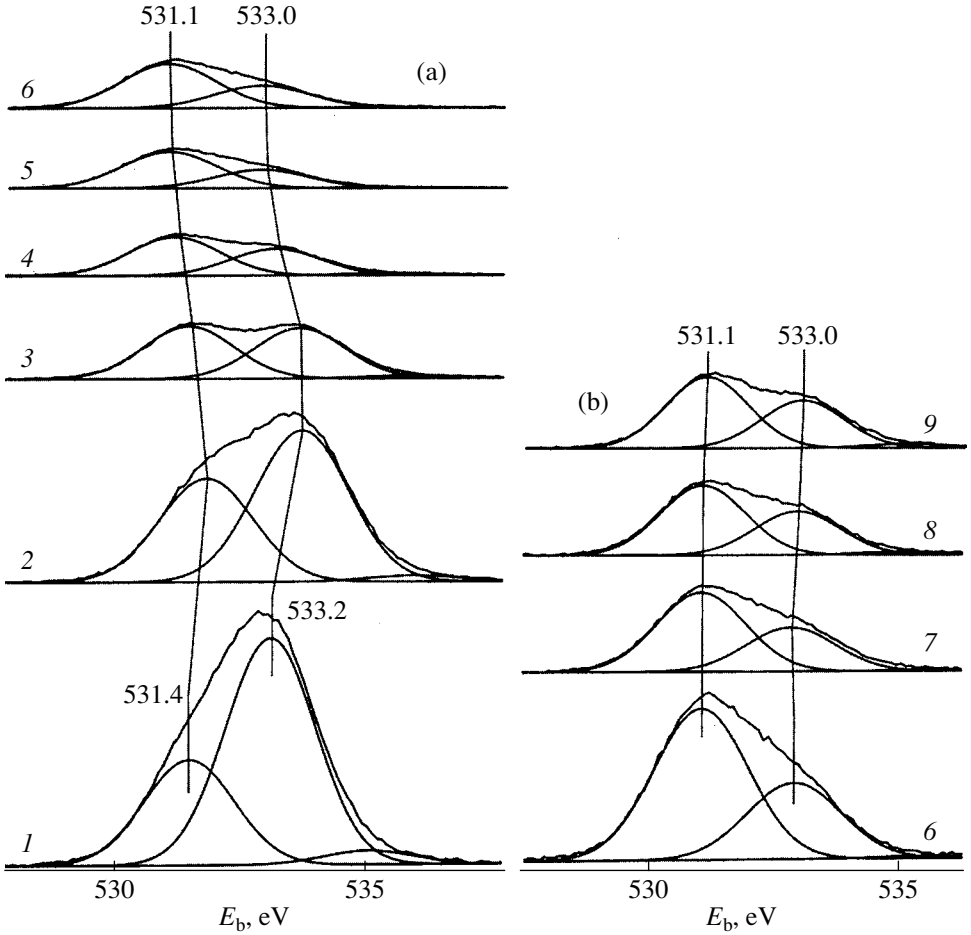


Fig. 2. O1*s* spectra of the surface of promoted silver foil in the course of (a) heating and (b) cooling: (*1*) 333, (*2*) 423, (*3*) 573, (*4*) 723, (*5*) 873, (*6*) 923, (*7*) 773, (*8*) 623, and (*9*) 473 K.

Heating not only shifts the O1*s* peaks but also changes their integral intensities (Fig. 2). Before heating, the spectrum is dominated by the higher energy peak, which is assigned to the terminal oxygen of the P=O group. Raising the temperature results in intensity redistribution between the spectrum components: the amount of bridging oxygen atoms of the Ag–O–P and P–O–P groups becomes two times greater than the amount of terminal oxygen atoms. This effect can be caused by the following:

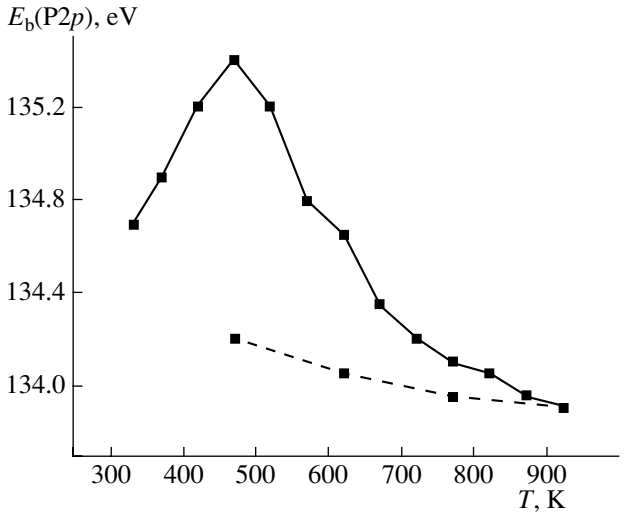
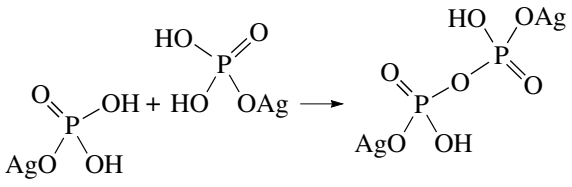


Fig. 3. P2*p* peak position as a function of sample temperature (solid line, heating; dashed line, cooling).

First, the desorption of water molecules results in a decrease in the amount of P–O–H bonds as a result of the polycondensation of silver hydrophosphate according to the following scheme:



Second, the migration of silver ions to the phosphorus-containing layer leads to an increase in the amount of Ag–O–P groups:

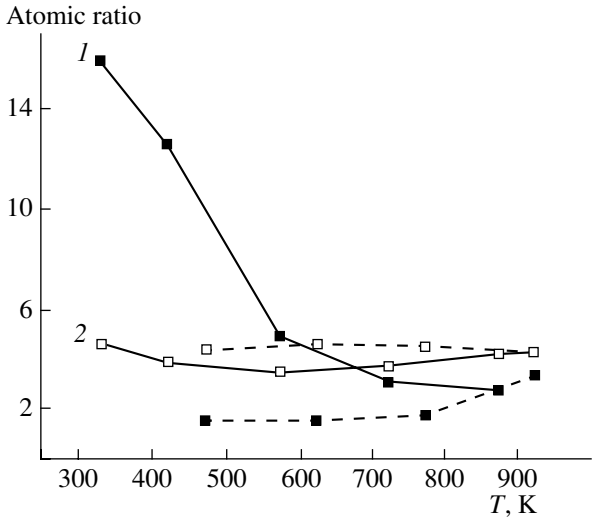


Fig. 4. (*1*) O : Ag and (*2*) O : P atomic ratios as a function of sample temperature (solid line, heating; dashed line, cooling).

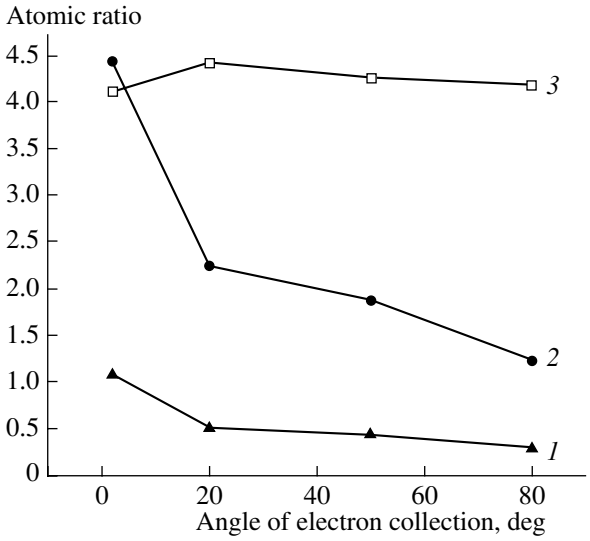
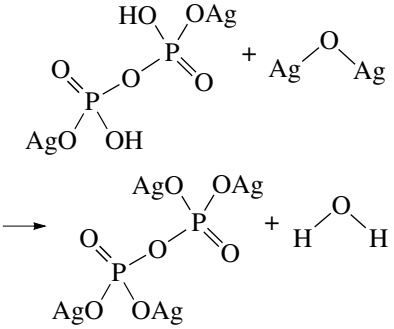


Fig. 5. (*1*) P : Ag, (*2*) O : Ag, and (*3*) O : P atomic ratios in the subsurface layers of the silver foil (ARXPS data).



It follows from Fig. 4, which plots the atomic ratios of oxygen to silver and phosphorus, that the treatment of silver foil with H_3PO_4 markedly increases the oxygen content on the sample surface compared to that of the untreated foil. The O : Ag atomic ratio decreases during heating of silver (Fig. 4, curve *1*) because of the decrease in the amount of oxygen on the sample surface due to the formation and desorption of H_2O and CO_2, as well as the diffusion of silver atoms from the bulk to the surface. The removal of water contributes only slightly to the variation of the O : Ag ratio, because the amount of oxygen atoms relative to phosphorus (O : P) changes little (Fig. 4, curve *2*). Comparing the data presented in Figs. 2 and 4 suggests that the greatest contribution to the change in the O : Ag ratio is made by silver diffusion to the surface of the polyphosphate film.

Cooling the sample from 923 to 473 K does not cause any essential change in the state of the major elements on the surface (Figs. 2b, 3, 4). The O1*s* and P2*p* lines shift to higher binding energies. This fact is likely to be due to the decrease in the silver content of the surface layer (Figs. 3, 4). This indicates that heating the silver foil treated with phosphoric acid results in the formation of a stable structure similar to silver polyphosphate. This structure has new properties essentially independent of temperature. Most of the oxygen on the foil surface is in two states with the binding energies 531.1 and 533.0 eV, and the amount of bridging oxygen of the Ag–O–P and P–O–P groups is nearly twice as large as the amount of terminal oxygen of the P=O group. It is obvious that the presence of a significant amount of bridging oxygen is the main factor in the high thermal stability of phosphorus-containing structures on the surface of silver foil.

The distribution of elements in the subsurface layers governs the properties of the system examined. To obtain element distribution data for the doped sample of silver foil, we recorded angle-resolved photoelectron spectra (ARXPS). In this method, the angle between the sample surface and the analyzer axis (take-off angle) is varied [4]. The ARXPS data are presented in Fig. 5. When the take-off angle is decreased, the O : Ag and P : Ag ratios increase, indicating that the spectra obtained at take-off angles close to 90° refer to both the phosphorus-containing film and the underlying bulk silver. Since electron emission was excited by soft X-ray radiation, AlK_α, the thickness of the phosphorus-containing film studied did not exceed ~60–90 Å. We estimated the thickness of the polyphosphate film under the assumption that the film is continuous, making use of the fact that the core lines of silver are screened by the phosphate film. Since the mean free path of electrons, λ, is 20–25 Å [4], the formula

$$d = -\lambda \ln \frac{I}{I_0},$$

where I_0 and I are the integral intensities of the Ag3*d* line before and after the deposition of orthophosphoric acid, gives a film thickness of d = 35–45 Å. The phosphorus content of the sample surface derived from

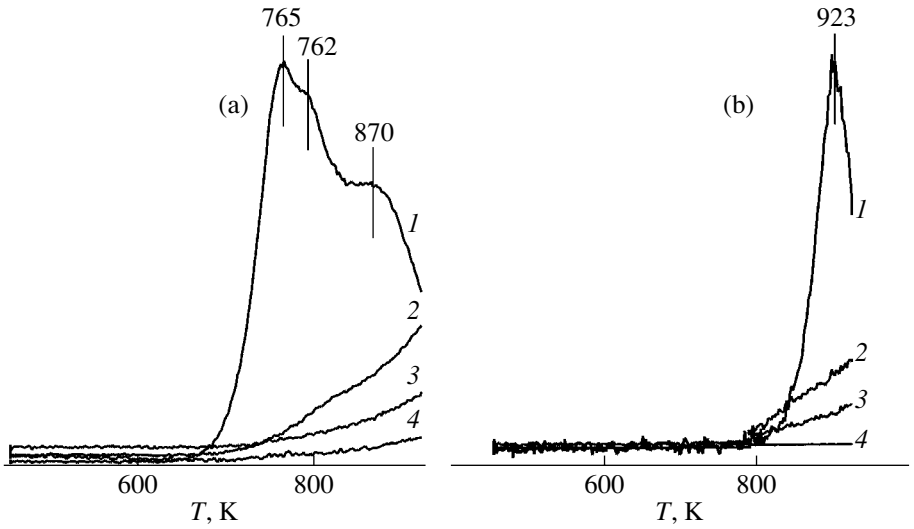


Fig. 6. Oxygen TDS spectra of the silver foil (a) before and (b) after promotion (treatment with O_2 in the spectrometer chamber for 10 h; P_{O_2} = 400 Pa; T = 673 K): (*1*) O_2, (*2*) CO_2, (*3*) CO, and (*4*) H_2O.

quantitative surface composition data for the phosphated Ag foil is P : Ag ≈ 1.

As can be seen in Fig. 5, varying the exit angle does not affect the O : P ratio. This indicates that almost all the oxygen and phosphorus atoms are chemically bonded to one another; that is, most of the oxygen is located in the uppermost layer of the sample. In addition, this finding accounts for the absence of oxygen species characteristic of the original foil in the spectra of samples treated with phosphoric acid and annealed at temperatures up to 923 K (Fig. 1a). The fact that most of the oxygen atoms are coordinated to phosphorus atoms is likely to be due to the phosphorus affinity of oxygen exceeding its silver affinity [17].

Figure 6 presents thermal desorption spectra for the original (Fig. 6a) and phosphated silver foils (Fig. 6b). As can be seen in Fig. 6, the main desorption product is oxygen. The appearance of trace amounts of CO_2 and CO in the TDS products is due to the desorption of these compounds from the walls of the spectrometer chamber. The oxygen thermal desorption spectrum of the phosphorus-free foil has several peaks, which, according to previous studies [11, 12, 18, 19], are due to the desorption of oxygen dissolved in the sample bulk, O_β, and strongly bound oxygen, O_γ. Oxygen desorption from silver treated with phosphoric acid does not occur in the temperature range of 450–800 K, indicating the absence of relatively weakly bound oxygen species on the surface. However, intensive oxygen desorption is observed starting at 800 K and up to 923 K. To avoid sample destruction, the temperature was not increased further in recording TDS. Thus, the phosphorus-containing sample is characterized by an oxygen thermal-desorption spectrum differing from that of the original silver foil. This is apparently due to the specific features of the morphology and electronic and geometric structures of the surface of the phosphated sample.

Note that treatment of the surface of the phosphated sample with oxygen for 30 or 120 min (P_{O_2} = 400 Pa, T = 673 K) followed by cooling in an oxygen atmosphere at a rate of 0.3 K/min, pumping, and heating from 473 to 923 K does not give rise to any oxygen desorption spectrum. Oxygen desorption is observed only after the phosphated sample is held in the O_2 atmosphere (P_{O_2} = 400 Pa, T = 673 K) for 10 h (Fig. 6). Since the heating of the freshly phosphated Ag foil before oxygen treatment is accompanied by the desorption of only H_2O and negligible amounts of CO_2 (in the temperature range 473–593 K), it is impossible to explain the presence of the oxygen peak in the thermal-desorption spectrum (Fig. 6) by the decomposition of silver phosphate. Furthermore, silver phosphate melts without decomposition at 1122 K [20].

According to [21], the solubility of oxygen in silver phosphate is close to zero. At the same time, according to the above data, silver dissolves in phosphate in excess of the stoichiometric ratio, being distributed as both separate atoms and clusters in the subsurface layers of the sample. Ziyad *et al.* [2] drew a similar conclusion from their study of the behavior of the mixed salt $AgTh_2(PO_4)_3$ in the oxidative dehydrogenation of 2-butanol.

When oxygen interacts with the surface of phosphorus-containing foil, silver clusters are likely to interact with oxygen. This oxygen–silver interaction produces no oxide: no corresponding oxygen peak in the E_b range ~529–530 eV is observed in the O1*s* spectrum (Fig. 1) [12, 13]. This fact is evidence of the formation of a new oxide structure, Ag_xO_y, surrounded by phosphorous,

under these conditions. Oxygen in this structure is less nucleophilic and thermally much more stable than in Ag_2O. The exact composition of this structure is to be estimated with the use of appropriate techniques. Thus, one can assume that oxygen is evolved by Ag_xO_y structures that have cropped out to the foil surface. However, Ag_xO_y structures form slowly under the conditions examined, apparently because of the low diffusivity of the Ag clusters in the phosphate layer.

Figure 7 presents the Ag-MNN Auger spectra of the phosphorus-containing silver foil. After the thermal treatment of the sample at 473, 923, and 473 K in succession (Fig. 7, curve *1*), the Ag-MNN spectrum contains two bands assigned to metallic silver and to silver atoms included in the phosphate structure [4]. The presence of metallic silver in the sample heated up to 923 K indicates that the Ag clusters are formed in the phosphate film.

After the sample had been treated with oxygen (P_{O_2} = 400 Pa, T = 673 K, 10 h), metallic silver was not detected (Fig. 7, curve *2*). Hence, the clusters lose their metallic properties when interacting with oxygen to form Ag_xO_y. After the thermal desorption run, the metallic silver band is again observed in the spectrum (Fig. 7, curve *3*); that is, the sample has returned to the original state.

Thus, oxygen diffusion in the phosphorus-containing layer occurs through the formation of Ag_xO_y structures upon the interaction between gaseous oxygen and silver clusters distributed in the subsurface region of the polyphosphate film.

We showed previously [22] that the oxidation of ethylene glycol to glyoxal over electrolytic silver crystals is the most selective at 823 K. At the same time, according to [23], the phosphoric acid promoted silver catalyst is most active in the glyoxal synthesis at higher temperatures (the optimum temperature is T = 900 K). This result is in good agreement with the TDS data obtained in this work, which point to the fact that the oxygen species formed in the phosphate matrix with the participation of Ag clusters are thermally more stable as compared to the high-temperature oxygen species on the polycrystalline surface of bulk silver. The finding that the peaks due to the low-temperature oxygen species are missing from the TDS spectrum explains the enhanced selectivity of promoted silver [23], since it is the less strongly bound oxygen species on the catalyst surface that are responsible for the side processes resulting in the deep oxidation of ethylene glycol.

Several cycles of treatment of the promoted silver foil, including oxygenation followed by heating to 923 K, demonstrated that the state of the sample surface remains unchanged and stable at all treatment stages. One can assume that the increase in the lifetime of the H_3PO_4-promoted silver catalysts for ethylene glycol oxidation [3, 23] is due to the high stability of the phosphate film towards high-temperature reaction media. Furthermore, the glyoxal formation selectivity is increased because of the increased active oxygen content of the silver clusters on the surface of the promoted catalyst.

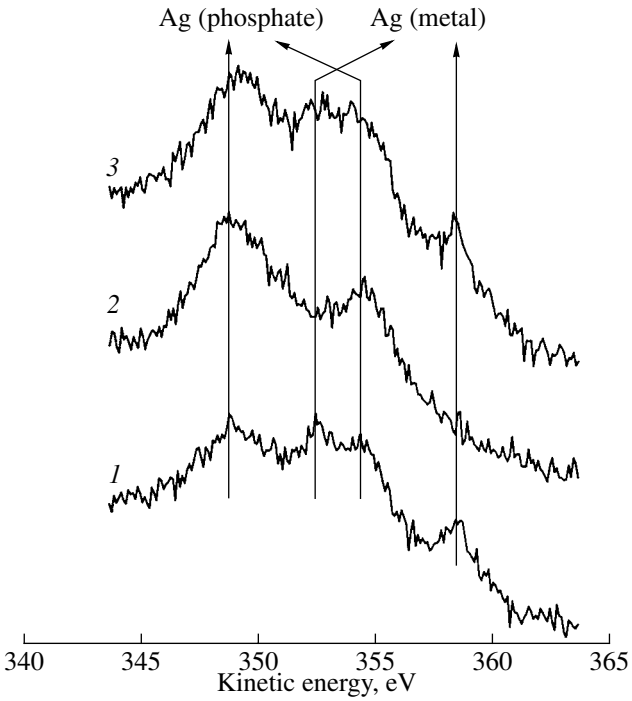


Fig. 7. Ag-MNN spectra of the phosphorus-containing silver foil: (*1*) sample heat-treated at 473, 923, and 473 K in succession; (*2*) the same sample after treatment with O_2 for 10 h (P_{O_2} = 400 Pa, T = 673 K); (*3*) the latter sample after a TDS run.

CONCLUSIONS

The interaction between silver foil and phosphoric acid results in the formation of a polyphosphate film on the silver surface. The chemical state of oxygen on the surface of unpromoted foil differs from that on phosphorus-containing silver. The treatment of the foil surface with phosphoric acid eliminates the lines due to adsorbed and oxide-like oxygen from the O1*s* spectrum and brings about two new oxygen states assignable to the bridging oxygen of the Ag–O–P and P–O–P groups and to the terminal oxygen of the P=O group. High-temperature treatment results in restructuring of the promoter layer to increase the amount of bridging oxygen.

Silver on the surface of the phosphorus-containing foil is in two states, namely, metal and phosphate. An overstoichiometric amount of silver is present in the surface layer of the phosphate film. Upon treatment of the sample with oxygen, metallic silver disappears because of the formation of oxide structures of the Ag_xO_y type. Heating the silver foil decomposes the Ag_xO_y clusters to yield metallic silver.

The Ag_xO_y structures form through migration of silver clusters to the sample surface followed by the interaction between these clusters and gaseous oxygen. The state of oxygen bound to the silver cluster differs from the state of oxygen in Ag_2O because of the effect of the environment of the silver cluster in the phosphorus-containing matrix.

The data obtained in this work correlate with the results of earlier studies on the partial oxidation of ethylene glycol to glyoxal over an Ag catalyst promoted with phosphorus-containing compounds. The increase in the lifetime of the H_3PO_4-promoted silver catalysts for ethylene glycol oxidation is a consequence of the high stability of the promoting layer toward high-temperature reaction media, and the enhancement of glyoxal formation selectivity is due to the increased active oxygen content of the silver clusters on the surface of the promoted Ag catalyst.

ACKNOWLEDGMENTS

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REFERENCES

1. Brailovskii, S.M., Temkin, O.N., and Trofimova, I.V., *Probl. Kinet. Katal.*, 1985, vol. 19, p. 146.
2. Ziyad, M., Arsalane, S., Kacimi, M., Coundurier, G., Millet, J.-M., and Vedrine, J.C., *Appl. Catal. A*, 1996, vol. 147, no. 3, p. 363.
3. Deng, J.F., Wang, J., and Xu, X., *Catal. Lett.*, 1996, vol. 36, no. 1, p. 207.
4. *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, Briggs, D. and Seah, M.P., Eds., New York: Wiley, 1983.
5. Boronin, A.I., Bukhtiyarov, V.I., Vishnevskii, A.L., Boreskov, G.K., and Savchenko, V.I., *Surf. Sci.*, 1988, vol. 201, no. 3, p. 195.
6. Bukhtiyarov, V.I., Boronin, A.I., and Savchenko, V.I., *J. Catal.*, 1994, vol. 150, no. 2, p. 262.
7. Moulder, J.F., Stickle, W.F., Sobol, P.E., and Bomben, K.D., *Handbook of X-ray Photoelectron Spectroscopy*, Eden Prairie: Perkin-Elmer, 1992.
8. Lefferts, L., van Ommen, J.G., and Ross, J.R.H., *Appl. Catal.*, 1986, vol. 23, no. 3, p. 385.
9. Boronin, A.I., Koscheev, S.V., Malakhov, V.F., and Zhidomirov, G.M., *Catal. Lett.*, 1997, vol. 47, no. 1, p. 111.
10. Boronin, A.I., Koscheev, S.V., and Zhidomirov, G.M., *J. Electron. Spectrosc. Relat. Phenom.*, 1998, vol. 96, no. 1, p. 43.
11. Nagy, A. and Mestl, G., *Appl. Catal. A*, 1999, vol. 188, no. 3, p. 337.
12. Bao, X., Muhler, M., Schedel-Niedrig, Th., and Schlogl, R., *Phys. Rev. B: Condens. Matter*, 1996, vol. 54, p. 2249.
13. Boronin, A.I., Koscheev, S.V., Murzakhmetov, K.T., Avdeev, V.I., and Zhidomirov, G.M., *Appl. Surf. Sci.*, 2000, vol. 165, no. 1, p. 9.
14. Syutkin, V.M. and Tolkatchev, V.A., *Chem. Phys.*, 1996, vol. 212, no. 1, p. 149.
15. Cutroni, M., Mandanici, A., MustarellI, P., Tomasi, S., and Federico, M., *J. Non-Cryst. Solids*, 2002, vols. 307–310, no. 5, p. 963.
16. Matic, A., Swenson, J., Borjesson, L., Longeville, S., Lechner, R.E., Howells, W.S., Akai, T., and Martin, S.W., *Physics B*, 1999, vol. 266, no. 1, p. 69.
17. Nekrasov, B.V., *Osnovy neorganicheskoi khimii* (Fundamental Inorganic Chemistry), 1970, vol. 3.
18. Vodyankina, O.V., Kurina, L.N., Sudakova, N.N., and Izatulina, G.A., *Zh. Fiz. Khim.*, 1998, vol. 72, no. 3, p. 521.
19. Rehren, C., Isaac, G., Schlogl, R., and Ertl, G., *Catal. Lett.*, 1991, vol. 11, no. 2, p. 253.
20. Goronovskii, I.T., Nazarenko, Yu.P., and Nekryach, E.F., *Kratkii spravochnik po khimii* (Concise Handbook of Chemistry), Kiev: Naukova Dumka, 1974, p. 66.
21. Fromm, E. and Gebhart, E., *Gazy i uglerod v metallakh* (Gases and Carbon in Metals), Moscow: Metallurgiya, 1980.
22. Vodyankina, O.V., Kurina, L.N., Boronin, A.I., and Salanov, A.N., *Stud. Surf. Sci. Catal.*, vol. 130, no., p. 1775.
23. Knyazev, A.S., Sushkova, E.V., Vodyankina, O.V., Salanov, A.N., Shmotin, V.S., Shilyaeva, L.P., and Kurina, L.N., *Neftekhimiya*, 2003, vol. 43, no. 6, p. 454.