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Role of Phosphates in Promotion of Silver Catalysts for Partial Oxidation: II. Formation of Active Sites in the Structure of Silver Phosphate under the Action of a Reductive Medium

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Abstract—The morphology and chemical composition of the surface of silver phosphate are studied. The qualitative and quantitative compositions of silver phosphate are quite the same as those of the surface of the phosphorus-promoted silver catalyst. Silver particles surrounded by silver phosphate form in the subsurface region upon treatment of the sample with hydrogen. As a result, a complex catalytic system is formed in which silver phosphate is both the precursor of the reactive component (metallic silver particles) and the stabilizing matrix for this component. The system obtained is stable toward high temperature and redox reaction media.

Phosphorus-containing salts of *d*-metals are widely used in catalytic systems for oxidation of organic compounds. For instance, the catalysts $FePO_4$, $(VO)_2P_2O_7$, $H_3PMo_{12}O_{40}$ are used for partial oxidation of alkanes, alkenes, alcohols, aldehydes, and acids [1–5]. Phosphorus-containing compounds are employed as promoters for metallic catalysts for partial oxidation of ethylene glycol [6, 7]. The mechanism of catalysis by metal phosphates is not well understood. There have been assumptions as to the role of oxygen bonded to the metal atom, which is capable of incorporating into an oxidized molecule [1].

It was assumed for phosphorus-modified metallic silver catalysts for partial oxidation of ethylene glycol that the promoter reduces the amount of C_1 deep-oxidation products by strengthening the bond between adsorbed oxygen and the silver surface [6, 8]. However, the cause of the high catalytic activity of phosphoric acid salts in the processes of partial oxidation of organic compounds has not been completely understood up to now.

Earlier, we showed that, after the treatment of silver foil with phosphoric acid, silver occurs on the sample surface in two states, specifically, as metal and phosphate [9]. It was assumed that metallic silver is present as clusters in the phosphate film.

In this work, the processes occurring in silver phosphate treated with a reductive medium were characterized by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The data obtained provide a deep insight into the processes occurring on the surface of catalysts based on silver phosphate and on the surface of model catalytic systems modified with phosphorus-containing compounds.

EXPERIMENTAL

Silver phosphate was prepared by precipitation from a solution of ammonium hydrogen phosphate mixed with silver nitrate. The ammonium cation was removed by calcination of the salt in an N_2 atmosphere at 823 K for 1 h. The freshly calcined product appeared as a yellow crystalline powder.

Surface composition was determined by XPS. The photoelectron spectra of silver catalysts were recorded on a VG ESCALAB spectrometer (the procedure was described in detail in [10–12]). The samples were supported on a tantalum plate by depositing salt powder from an alcoholic suspension followed by drying in air. Before spectroscopic measurements, the samples were pumped in the pretreatment chamber down to $P = 10^{-7}$ Pa and transferred to the analyzer chamber with a base vacuum of 10^{-8} Pa. The main background gases were CO, CO_2, and H_2O. The samples were treated with hydrogen *ex situ* at $T = 473$–823 K for 20–120 min (10% H_2/N_2) and in the pretreatment chamber of the spectrometer at $P_{H_2} = 10$–500 Pa, $T = 473$ and 573 K, varying the treatment time from 20 min to 9 h; 99.9% pure hydrogen was used. After reduction, the sample was heated *in vacuo* at 723 K for 30 min. The heating rate in the spectrometer chamber was 1 K/min. XPS spectra were recorded at the sample-treatment temperature.

Spectroscopic data were processed using standard graphical packages and the special-purpose program

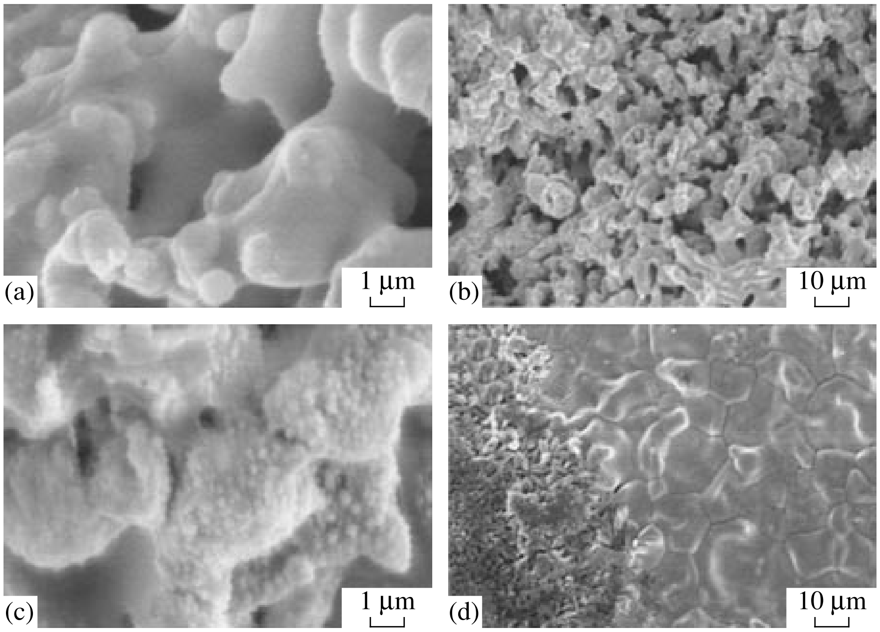


Fig. 1. Surface morphology of (a, b) freshly calcined silver phosphate and (c, d) the same sample after treatment with 10% $H_2 + N_2$ (c) at $T = 473$ K for 20 min and (d) at $T = 823$ K for 120 min.

CALC. To estimate the chemical composition, the most intense lines of elements were precisely recorded. The concentration ratio of components in the sample was derived from the integrated intensities of the lines from the corresponding atomic levels, taking into account the tabulated empirical atomic sensitivity factors [13].

The surface morphology of the silver phosphate samples was studied by SEM on a BS-350 field-emission high-vacuum scanning electron microscope (Tesla) with a primary electron beam energy of 16 kW. To increase the image contrast, a 0.05-μm-thick gold film was deposited onto the sample surface.

RESULTS AND DISCUSSION

Figures 1a and 1b present the surface morphology of silver phosphate crystals calcined at 823 K. This sample is characterized by a developed surface consisting of separate agglomerates ~1–3 μm in size, which form a sponge structure (Fig. 1a). The volume of voids is comparable to the volume of the solid phase. According to XPS data for the sample surface, the salt contains no foreign impurities and its composition is given by the formula $Ag_2HPO_4 \cdot 0.5H_2O$ (table). Note that the chemical composition of the silver phosphate surface is similar to that of the Ag foil surface treated with H_3PO_4 [9]. This allows us to compare the data obtained for these systems.

An overstoichiometric amount of oxygen in the calcined salt (table) was also found in a previous study of the phosphate film on polycrystalline silver foil [9]. The overstoichiometric oxygen can be due to the presence of water molecules in the phosphate structure. Water in the closed pores of the salt structure is completely desorbed upon thermal treatment.

The second factor responsible for the overstoichiometric oxygen on the surface of the samples is carbon–oxygen structures resulting from the adsorption of atmospheric carbon-containing compounds when the sample is transferred to the spectrometer chamber.

Relative atomic concentrations of elements on the surface of silver phosphate samples before and after hydrogen treatment

No.	Sample	Relative atomic concentrations		
		C/Ag	O/Ag	P/Ag
1	Freshly prepared Ag_2HPO_4	0.63	2.61	0.56
2	Reduced ($P_{H_2} = 100$ Pa, $T = 473$ K, 20 min)	0.47	1.92	0.42
3	Reduced ($P_{H_2} = 500$ Pa, $T = 573$ K, 9 h)	0.31	1.59	0.33
4	Heated in a vacuum after hydrogen treatments ($T = 723$ K, 30 min)	0.15	2.42	0.58

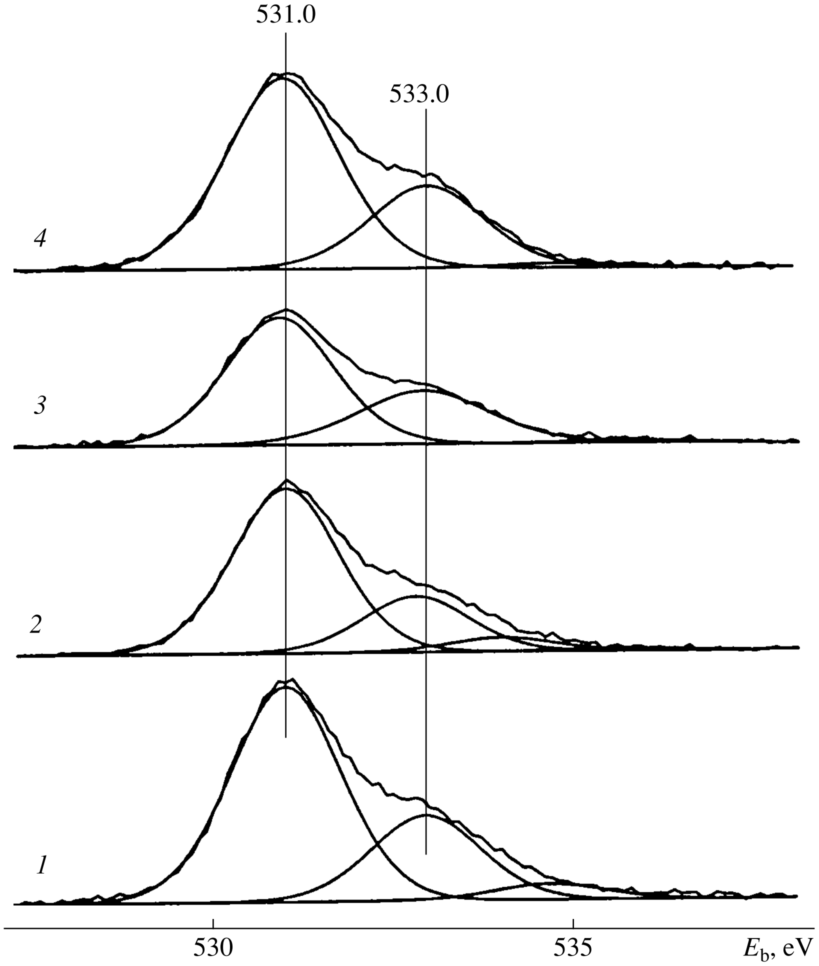


Fig. 2. O1*s* photoelectron spectra of silver phosphate samples: (*1*) freshly calcined, (*2*) after treatment with H_2 (H_2 (P_{H_2} = 100 Pa, T = 473 K, 20 min), (*3*) after treatment with H_2 (P_{H_2} = 500 Pa, T = 573 K, 9 h), and (*4*) annealed *in vacuo* (723 K, 30 min) after reduction with hydrogen. $I_{531.0}/I_{533.0}$ = (*1*) 2.56, (*2*) 2.30, (*3*) 2.00, and (*4*) 2.31.

According to detailed C1*s* spectroscopic data (not shown here), carbon on the sample surface is in a partially oxidized state. In view of this, the contribution of carbon–oxygen species to the O1*s* spectrum was not taken into account in the calculation of the qualitative and quantitative compositions of the salts.

Figure 2 (sample *1*) presents the O1*s* spectrum of the surface of silver phosphate calcined at 823 K. The deconvolution of the spectrum showed that two main oxygen states with electron binding energies E_b(O1*s*) = 531.0 and 533.0 eV are present on the sample surface and they are identical to those found in a phosphate film supported on the surface of silver foil [9]. The E_b(O1*s*) = 531.0 eV peak was assigned to the bridging oxygen of the Ag–O–P, P–O–P, and P–O–H groups. The other major species, with E_b(O1*s*) = 533.0 eV, is the terminal oxygen of the P=O groups. The domination of the first species indicates a high extent of polymerization of silver phosphate.

It was shown earlier that the oxygen treatment of the phosphate film surface does not substantially change its structure or chemical properties [9]. Study of the behavior of silver phosphate in a reductive atmosphere was an important task of this work. Reaction mixtures containing phosphates as catalysts or promoters possess both oxidative and reductive properties owing to the presence of both O_2 and organic compounds. To model the effect of a reductive reaction mixture on the catalyst, silver phosphate was treated with hydrogen.

The surface morphology of samples treated with hydrogen under various conditions is shown in Figs. 1c and 1d. Silver is partially reduced upon low-temperature treatment (T = 473 K) according to the equation $Ag^+ + H^0 \longrightarrow Ag^0 + H^+$ (Fig. 1c) and is distributed on the salt surface in the form of separate particles ~0.3 μm in size. Part of the sample surface remains unaffected. This inference was confirmed by Ag-MNN Auger spectroscopic data for this sample (Fig. 3, spec-

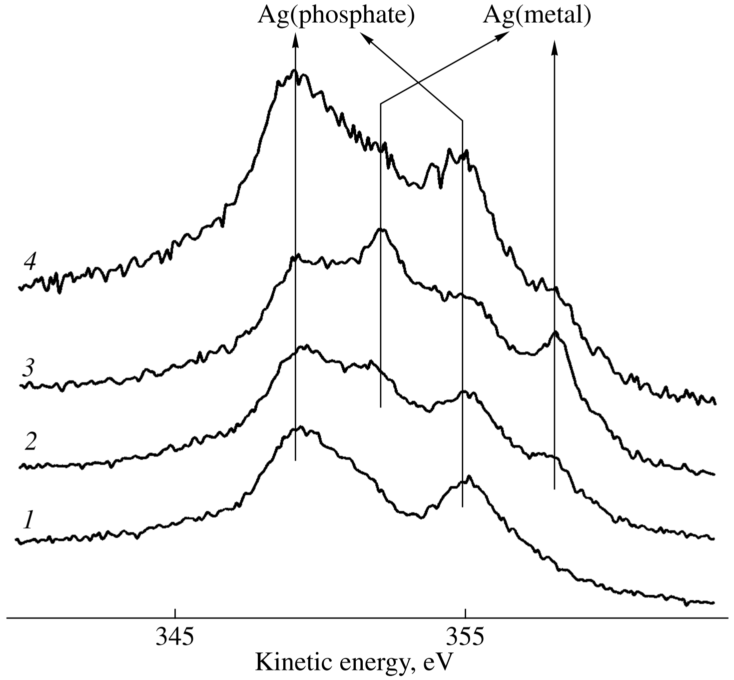


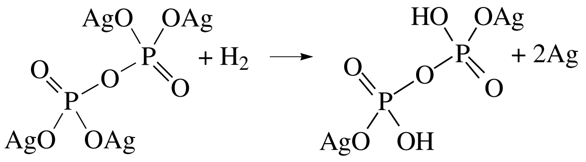
Fig. 3. Ag-MNN spectra of silver phosphate samples: (*1*) freshly calcined, (*2*) after treatment with H_2 (P_{H_2} = 100 Pa, T = 473 K, 20 min), (*3*) after treatment with H_2 (P_{H_2} = 500 Pa, T = 573 K, 9 h), and (*4*) calcined *in vacuo* (723 K, 30 min) after reduction with hydrogen.

trum *2*). The Auger spectrum of hydrogen-treated silver phosphate contains a metallic component that is absent from the spectrum of the original sample (Fig. 3, spectrum *1*). However, the spectral component due to the silver cations of the salt persists even after prolonged exposure of the sample to hydrogen (Fig. 3, spectrum *3*).

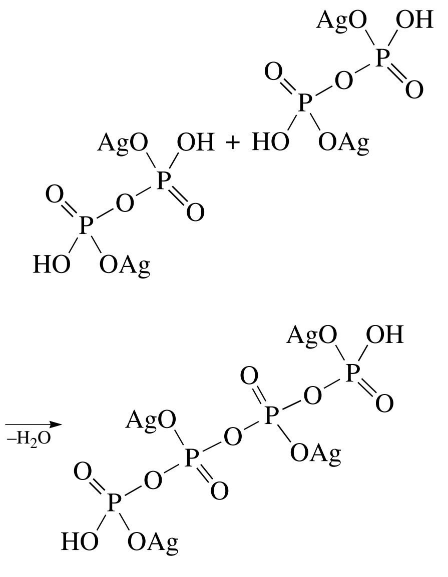
The decrease in the O : Ag and P : Ag atomic ratios according to quantitative analysis data for the reduced samples (table) also indicates that the concentration of metallic silver on the salt surface increases upon reduction. Hydrogen treatment of silver phosphate at 823 K for 2 h leads to the formation of close-packed crystallites of metallic silver with sizes of 5–15 μm (Fig. 1d). Furthermore, areas of the original silver phosphate are observed on the surface. However, their proportion on the surface of the reduced salt is negligible.

It is important that the O1*s* spectrum changes only slightly upon hydrogen treatment (Fig. 2, spectra *1–3*), and this leads to a conclusion as to the stability of the oxygen states on the sample surface. Only the ratio of the peak areas in the O1*s* spectrum changes to some extent. Estimating the ratio between the $E_b(\text{O}1s)$ = 531.0 and 533.0 eV areas showed that salt reduction with hydrogen causes a growth in the intensity of the $E_b(\text{O}1s)$ = 533.0 eV state (Fig. 2). This can be due to the increase in the water content of the sample surface, because the $E_b(\text{O}1s)$ = 533.0 eV component can be partly attributed to adsorbed water [10].

The increase in the number of strongly bound water molecules on the surface during hydrogen reduction can be due to the fact that the reduction of silver phosphate with hydrogen occurs in two stages:



(I)



(II)

At the first stage, the silver cations are reduced with hydrogen; at the second stage, the polycondensation of the P–O–H groups takes place upon high temperature treatment to form water molecules coordinated in the phosphate structure. These strongly bound molecules do not desorb in the temperature range examined. If only the reduction of Ag^+ (that is, the conversion of P–O–Ag groups to P–O–H groups) were observed, then the intensity of the O1*s* line at $E_b(O1s) = 533.0$ eV would not change.

After hydrogen treatment, heat treatment of silver phosphate for 30 min *in vacuo* at $T = 723$ K causes changes in the chemical composition of the salt surface that are opposite to those occurring during reduction. The intensities of the peaks assigned to metallic silver in the Ag-MNN Auger spectrum (Fig. 3, curve *4*) decrease. When the reducing agent is absent, the system likely returns to its original state: the silver clusters diffuse to the subsurface region, and, as a result, the surface of the annealed sample is dominated by silver polyphosphate. Changes in the O1*s* spectrum are also observed (Fig. 2, spectrum *4*). The 531.0- and 533.0-eV peak areas become close to the value observed for the untreated salt. This provides evidence of the stability of the system, which does not undergo irreversible processes in either an oxidative or a reductive medium.

Important properties of the system were determined by the layer-by-layer analysis of the salt after several reduction–calcination cycles, which model the effect of reaction mixtures used in catalytic processes. The results of the layer-by-layer analysis of silver phosphate are shown in Fig. 4. Quantitative calculations in the framework of the XPS method revealed that the depth profiles of phosphorus and silver have an extremum. The surface layers of the sample are characterized by an increased phosphorus content, which initially decreases with growing depth and then regains a high value.

The extrema in the depth profiles of the atomic ratios (Fig. 4) are evidence of the nonuniform distribution of silver in the subsurface layers of the sample. High temperature likely causes the diffusion of the silver clusters to the subsurface region.

Thus, the reduced and annealed sample is a complicated system. Its surface contains silver metal crystallites embedded in a phosphate layer, which prevents silver sintering at high temperatures.

This finding provides an explanation for the unique catalytic properties of metal phosphates. The reaction medium partially reduces the metal to form crystallites distributed in the phosphate matrix. The conversion of alcohols mediated by strongly bound oxygen species occurs on the surface of these Ag crystallites. The formation of electrophilic oxygen species on the silver surface modified with phosphorus-containing compounds was reported in [9]. The phosphorus-containing structures stabilize the dispersed state of silver in high-temperature catalytic processes.

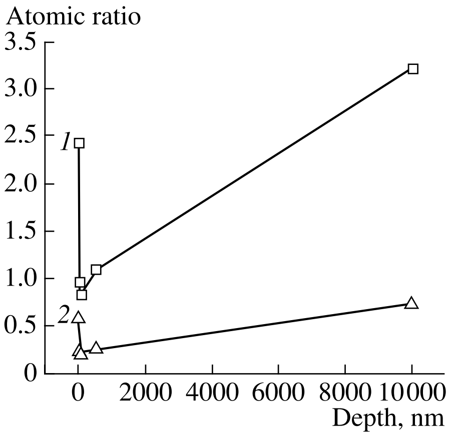


Fig. 4. Atomic ratio of elements in the structure of reduced silver phosphate after calcination *in vacuo* at $T = 723$ K for 30 min: (*1*) O : Ag and (*2*) P : Ag.

This study provides insight into the chemical properties of silver phosphate and into the effect of hydrogen treatment. The surfaces of the original and reduced catalysts contain oxygen in two states with binding energies of 531.0 eV (Ag–O–P and P–O–P bridges) and 533.0 eV (terminal P=O groups). Hydrogen treatment of silver phosphate at elevated temperature produces crystallites of metallic silver on the sample surface. The reductive atmosphere and high temperature produce a complicated system consisting of silver crystallites embedded in stoichiometric silver hydrophosphate, which prevents silver sintering.

Thus, a unique catalytic system is obtained in which silver phosphate serves as both the precursor of a reactive component (silver particles) and the stabilizing matrix for this component. Phosphate possesses the important property of high metal affinity, which prevents the sintering of the active component at high temperatures and, therefore, catalyst deactivation. The peculiarity of the phosphate–active component system is the high stability toward oxidative and reductive reaction media in a wide temperature range. The surface does not undergo irreversible changes upon either oxygen treatment or hydrogen reduction, returning to its original state after the external action is ceased.

Our studies resulted in the development of a new method for preparation of catalytic systems. This method includes pretreatment of the catalyst with a reaction mixture having certain redox properties and yields a complicated structure characterized by a high mutual chemical affinity of the components, namely, metal clusters and the stabilizing matrix.

This method is rather promising, because it allows easy variation of the amount of the active component and control of the physicochemical properties of the system at the preparation stage.

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