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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Supported Silver-containing Systems Based on Silicon Nitride

I. A. Kurzina, L. N. Chukhlomina, M. N. Gorlenko, and O. V. Vodyankina

Tomsk State Architectural and Construction University, Tomsk, Russia
Tomsk Scientific Center, Siberian Branch, Russian Academy of Sciences, Tomsk, Russia
Tomsk State University, Tomsk, Russia

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Abstract—Specific features of the structure, morphology, and phase composition, and also physicochemical and catalytic properties of silver-containing systems supported by silicon nitride were studied. The effect of structural features and phase composition of silicon nitride on the state of particles of supported silver was examined in relation to the conditions of support preparation by self-propagating high-temperature synthesis and introduction of the active component.

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The development of methods for synthesis of new materials with a desired set of physicochemical and service properties becomes increasingly topical. Wide opportunities in this area are furnished by the method of self-propagating high-temperature synthesis (SHS), which can produce materials with controlled structure and chemical and phase composition [1]. This process is widely employed in the technology of inorganic materials; it can be used to obtain powders and ceramic materials and to deposit coatings.

One of the most demanded ceramic materials in various industries is silicon nitride. Silicon nitride is a high-valence compound having two thermodynamically stable modifications: low-temperature (<1200°C) α-phase and high-temperature (>1500°C) β-phase [2]. Both modifications have a hexagonal structure with identical parameters a and b, whereas parameter c of the α-phase is twice that of the β-phase [3, 4]. The basic parameters of silicon nitride (S_{sp} = 1.5–66 $m^2 g^{-1}$), average particle size (0.1–10 μm), phase composition (α/β phase ratio), and thermomechanical properties strongly depend on the synthesis conditions.

The set of unique physicomechanical properties of silicon nitride predetermines the keen interest in extending the applicability area of ceramic materials based on Si_3N_4. For example, it has been shown that silicon nitride is promising for the use as a support for palladium catalysts for deep oxidation of methane at elevated temperatures [5, 6]. It was demonstrated that raising the fraction of the α-modification of Si_3N_4 and lowering the content of the amorphous fraction in the support material leads to a higher activity of Pd catalysts in the deep oxidation of methane. Thus, the nature of the support may be of key importance for modification of the catalyst properties.

In turn, the properties of a support are determined by its chemical prehistory, i.e., by its preparation method. Therefore, studying the effect of the support nature on the physicochemical properties of metallic systems supported on the silicon nitride is a topical task. Moreover, use of silicon nitride is also topical from the standpoint of revealing the fundamental aspects of formation of metallic particles on the surface of a highly heat-conducting ceramics stable against redox and(or) corrosive reaction media at elevated temperatures. Systems in the form of silver particles supported on Si_3N_4 can be used as catalysts for partial oxidation of ethylene glycol to glyoxal.

The aim of this study was to determine how structural features and phase composition of silicon nitride affect the state of supported silver particles, depending on the SHS conditions of support synthesis and introduction of the active component, and to

examine the materials obtained as catalysts for selective oxidation of ethylene glycol into glyoxal.

EXPERIMENTAL

We used silicon nitride sample synthesized by the SHS method as a support for silver particles. The basic features of the process for synthesis of silicon nitride by this method were described in [7, 8]. The self-propagating high-temperature synthesis of Si_3N_4 was performed in a constant-pressure installation with a working volume of 3 l and the maximum working pressure of up to 15 MPa. Industrial ferrosilicon (FS 75) and dust-like waste produced in its crushing (PUD 75) were used as raw materials. Cylindrical tubes 40–60 mm in diameter with a gas-permeable wall were charged with the starting alloy. The relative density of the samples was 0.4. The samples were burnt in the atmosphere of gaseous nitrogen [99.996 vol %, GOST (State Standard) 9293–74]. The nitrogen pressure was varied within the range 1–10 MPa. The samples were ignited with a powdered igniter mixture with a tungsten coil. After the combustion front crossed the sample, it was kept in nitrogen till complete cooling, and then the pressure was relieved and the SHS product was subjected to acid dressing to remove iron. The phase composition of the silicon nitride synthesized and its dispersity was controlled by the temperature mode of synthesis, which was varied by introduction of ammonium halide salts into the starting alloy.

The active component was deposited onto the surface of silicon nitride (5 wt %) by two methods. The first of these included fractional chemical reduction (FCR) of silver nitrate to silver particles with sodium borohydride on the support surface from a silver nitrate solution, followed by drying, with temperature raised from 60 to 90°C, and by calcination at 600°C in a flow of oxygen. The second method consisted in silver phosphate deposition (SPD) by reacting an ammonia complex of silver phosphate with the surface of silicon nitride, followed by drying at 60° C and calcination at 100 to 600°C in a flow of air at a heating rate of 10 deg min^{-1}.

The content of the active component on the support surface was monitored with a Quant'X X-ray fluorescence spectrometer (XFS). The phase composition and the structural parameters of the supports and silver-containing systems were studied by means of X-ray phase analysis on an XRD-6000 diffractometer with CuK_α radiation. The relative contents of phases in silicon nitride were found from the intensity ratios of the corresponding lines in X-ray diffraction patterns [5]. The structural features of the support and catalysts were examined by scanning electron microscopy (SEM) on Philips SEM 515 and Tescan LMU II electron microscopes and by transmission electron microscopy (TEM) on Philips CM 30.[1]

The catalytic activity of the synthesized systems in partial oxidation of ethylene glycol (EG) into glyoxal (GO) was studied in a flow-through catalytic installation with a fixed catalyst bed (inner diameter of the reactor 16 mm) [9]. The height of the catalyst bed was 20 mm; molar composition of the reaction mixture, $(CH_2OH)_2 : H_2O : O_2 : N_2 = 1.0 : 3.4 : 1.0 : 10.0$; time of contact, 0.06 s. The catalytic activity was studied in the temperature range 500–620°C.

Silicon nitride support. We used silicon nitride samples synthesized by the SHS method. To determine how the phase composition and the dispersity of the substrate affect properties of silver-containing systems, Si_3N_4 samples were synthesized in different temperature modes. The systems under study were controlled by introduction of ammonium halide salts into the starting alloy [7, 8]. The main parameters of the supports are listed in the table. XPA spectra of nitride systems with a supported silver-containing phase are shown in Fig. 1, because the substrate material has not been modified upon deposition of the active component.

Introduction of an ammonium chloride additive (1–10 wt %) into the starting ferrosilicon makes it possible to obtain a combustion product with varied ratio between the α- and β-modifications of silicon nitride [8]. By varying the ratio between the initial nitrogen pressure and the amount of ammonium chloride, it is possible to obtain nitrated ferrosilicon both with 100% β-Si_3N_4 and with an increased content of α-Si_3N_4 (up to 80%).

The first support for silver-containing catalysts (Si_3N_4-I) was prepared from a nitrated ferrosilicon burnt in the presence of 7% ammonium chloride under a pressure of 7 MPa. According to XPA data, this material contains two main thermodynamic phases of silicon nitride (α- and β-phases), with the content of α-

[1] The structural-phase state and morphological features of the samples under study were analyzed at the Common Instruments center of Tomsk State University.

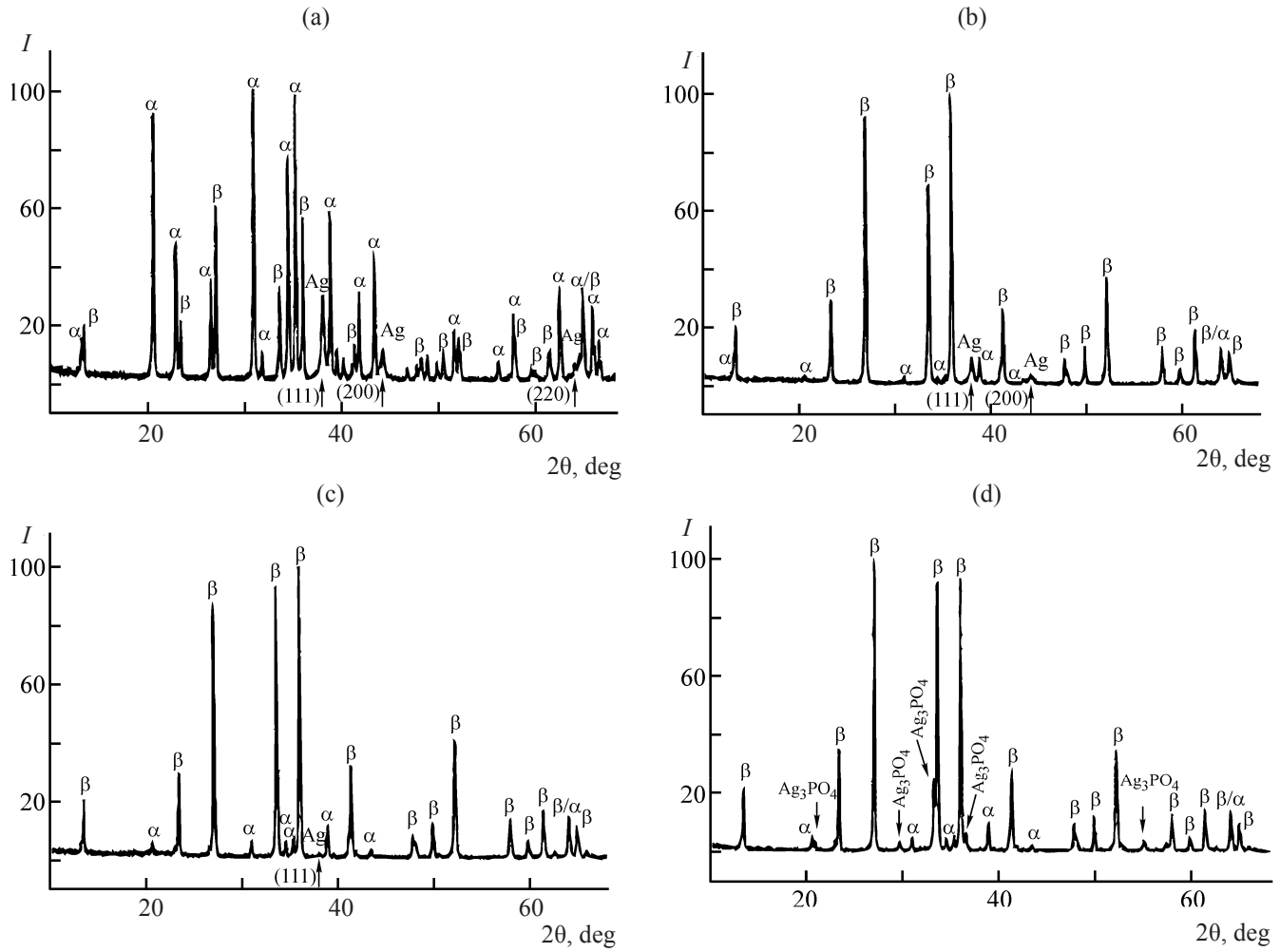


Fig. 1. XPA spectra of silver-containing systems supported on silicon nitride. (*I*) Intensity and (2θ) Bragg angle. (a) Ag/Si_3N_4-I, (b) Ag/Si_3N_4-II, (c) Ag/Si_3N_4-III, and (d) Ag–P–O/Si_3N_4-III.

Si_3N_4 being 75–80% at α/β ≈ 3 (see table, Fig. 1a). This support is a dispersed material with a particle size less than 2 μm and specific surface area of 6 $m^2\ g^{-1}$.

The second support (Si_3N_4-II) (see table), which is also a highly dispersed system, was obtained by combustion of ferrosilicon in the presence of ammonium fluoride. According to XPA data (Fig. 1b), the sample mostly contains (~95%) the high-temperature β-modification of silicon nitride. It should be noted that the content of α-Si_3N_4 could not be diminished to less than 5% by lowering the nitrogen pressure and the combustion temperature [8].

Si_3N_4-I and Si_3N_4-II samples produced with addition of ammonium chloride and ammonium fluoride strongly differ not only in the phase composition, but also in the surface morphology. Figure 2 shows SEM images of the surface of the Si_3N_4 materials used. The sample containing predominantly the α-phase (Si_3N_4-I) is composed of isometric columnar crystals and shapeless formations (Fig. 2a). The sample containing predominantly the β-phase (Si_3N_4-II) has "whiskers"-shaped particles (Fig. 2b). It is known that this shape is characteristic of the β-phase [5, 8]. The differences in the sample morphology are due to the synthesis conditions. Because reactions of nitride formation occur in the presence of ammonium chloride mainly in the gas phase in the low-temperature mode, the forming silicon nitride particles have considerably smaller sizes (Si_3N_4-I), compared with the case of fluorine-containing additives (Si_3N_4-II).

The third support (Si_3N_4-III) was produced by the SHS method without salt additives. A specific feature of silicon nitride synthesis from ferrosilicon is the

Main characteristics of silver-containing systems[a]

Sample	Characteristics of supports			Synthesis technique[b]	Ag content, wt %	K_{EG}, mol %	S_{GO}, mol %
	S_{sp}, m^2 g^{-1}	average particle size	phase composition, wt %				
Ag/Si_3N_4-I	6	1–2 μm	α ≈ 75–80	FCR	3.5	–	–
Ag/Si_3N_4-II	2	1 μm	β ≈ 95	FCR	2.0	–	–
Ag/Si_3N_4-III	2	0.5–1.0 mm	β ≈ 95	FCR	0.5	72.3	49.2
$Ag–P–O/Si_3N_4$-III				SPD	5.0	97.5	23.8

[a] K_{EG}, conversion of ethylene glycol; SGO, selectivity toward glyoxal.
[b] FCR, fractional chemical reduction of silver particles; S_{PD}, silver phosphate deposition.

presence of considerable amounts of an iron–silicon melt, which, on the one hand, accelerates the nitridation process and, on the other, causes filtration hindrance to nitrogen delivery to the reaction zone [8]. The presence of the melt favors further structural evolution behind the combustion front by providing conditions for collective recrystallization (further structuring) and for sintering of the synthesis products. The sintered SHS-nitrided ferrosilicon without salt additives is granulated to a required size by crushing. We used grains with an average size of 0.5–1.0 mm (see table, Fig. 1c). According to XPA and SEM data, the samples predominantly contain the β-phase (~85%); in addition, there are trace amounts of polymorphic silicon nitride modifications with tetragonal and orthorhombic crystal lattices [10].

According to the results of SEM studies, silicon nitride grains (Si_3N_4-III) are agglomerates of sintered cylindrical particles with broken edges and shapeless formations (Fig. 2c). The average size of such particles is 1–2 μm in a single direction. Treatment of the grains with a HCl solution to purify silicon nitride for removing iron results in that additional pores appear on the surface of a granulated Si_3N_4-III sample upon removal of iron impurities. A depression related to the

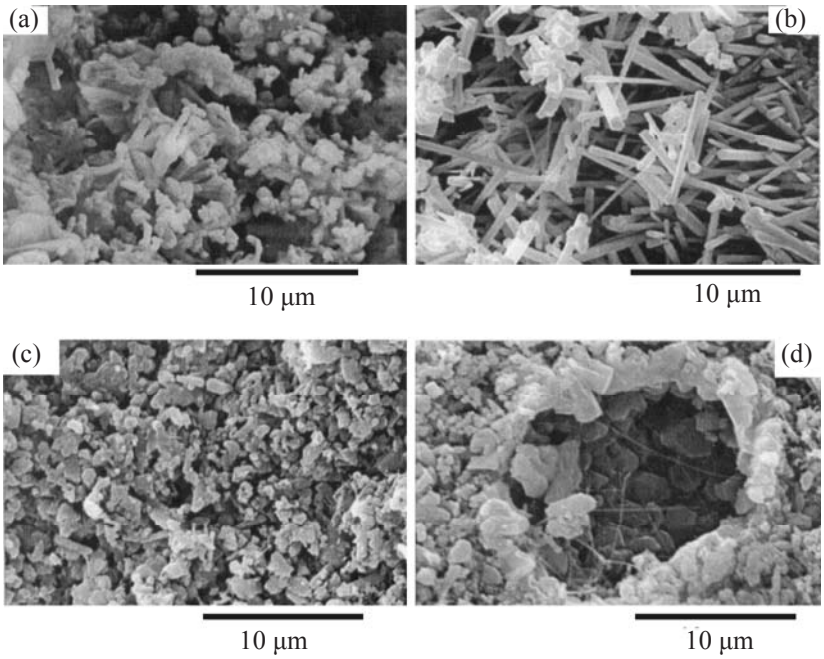


Fig. 2. SEM image of the surface of silicon nitride produced by combustion of ferrosilicon in nitrogen in the presence of (a) ammonium chloride (Si_3N_4-I), (b) ammonium fluoride (Si_3N_4-II) and (c, d) without salt additives (Si_3N_4-III).

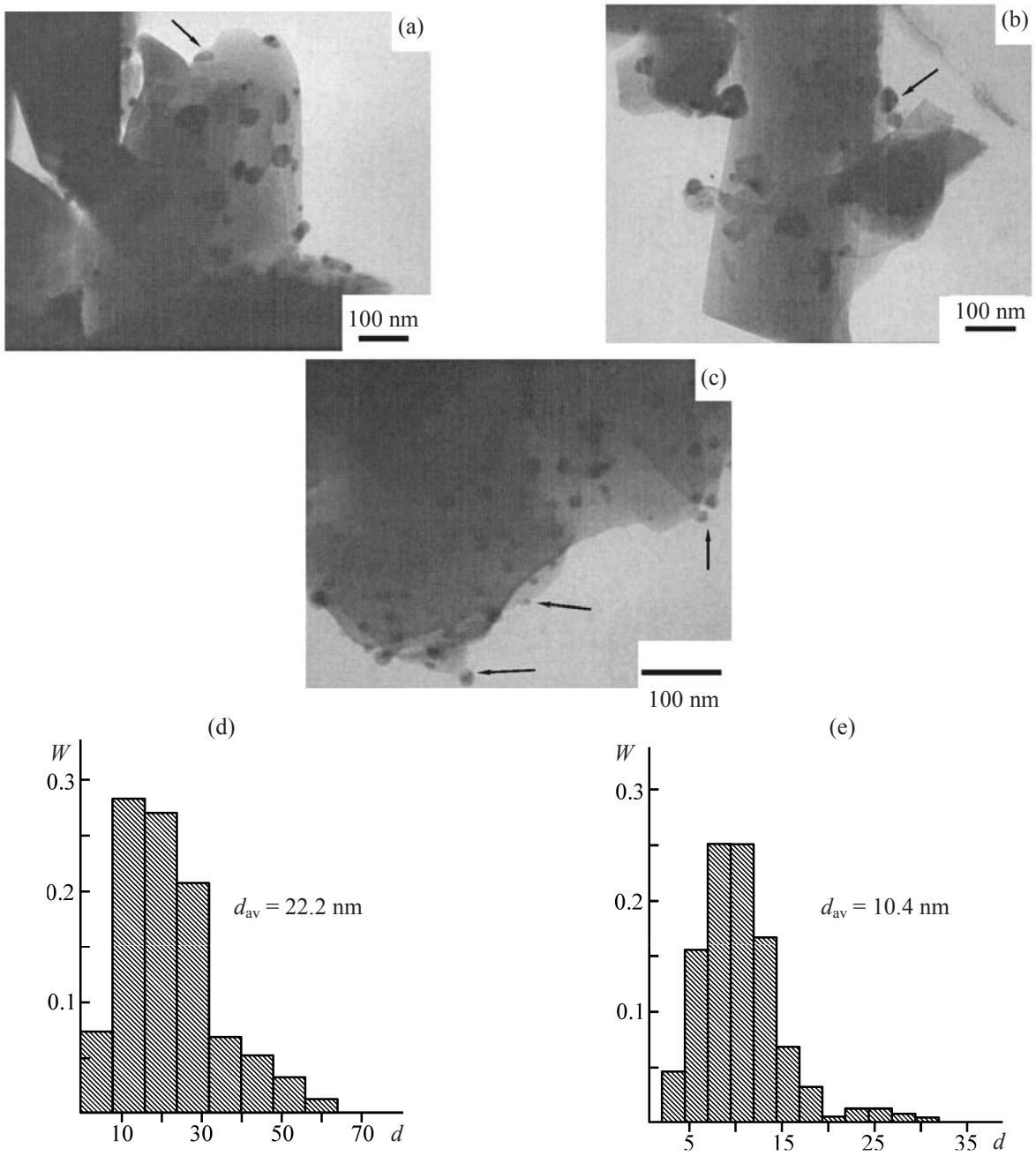


Fig. 3. (a–c) TEM images and (d, e) particle size distribution histograms of silver-containing systems supported by highly dispersed silicon nitride. (*W*) Fraction of particles and (*d*) particle diameter); the same for Figs. 4 and 5. (a, b, d) Ag/Si_3N_4-I and (c, e) Ag/Si_3N_4-II. Silver nanoparticles supported by silicon nitride are indicated by arrows.

presence of iron particles in the grains before the acid treatment is clearly seen in Fig. 2d. The specific surface area of silicon nitride grains is 1.8–2.0 $m^2 g^{-1}$.

Thus, three types of samples were used as supports in fabrication of silver-containing catalysts: dispersed silicon nitride particles synthesized in the presence of ammonium chloride (~80% α-Si_3N_4-I) and ammonium fluoride (~95% β-Si_3N_4, Si_3N_4-II) and grains synthesized without salt additives (~85% β-Si_3N_4, Si_3N_4-III).

Silver-containing Systems Based on Silicon Nitride

To analyze the influence exerted by the structural-phase composition of silver nitride on the formation of silver particles, we examined in the first stage of the

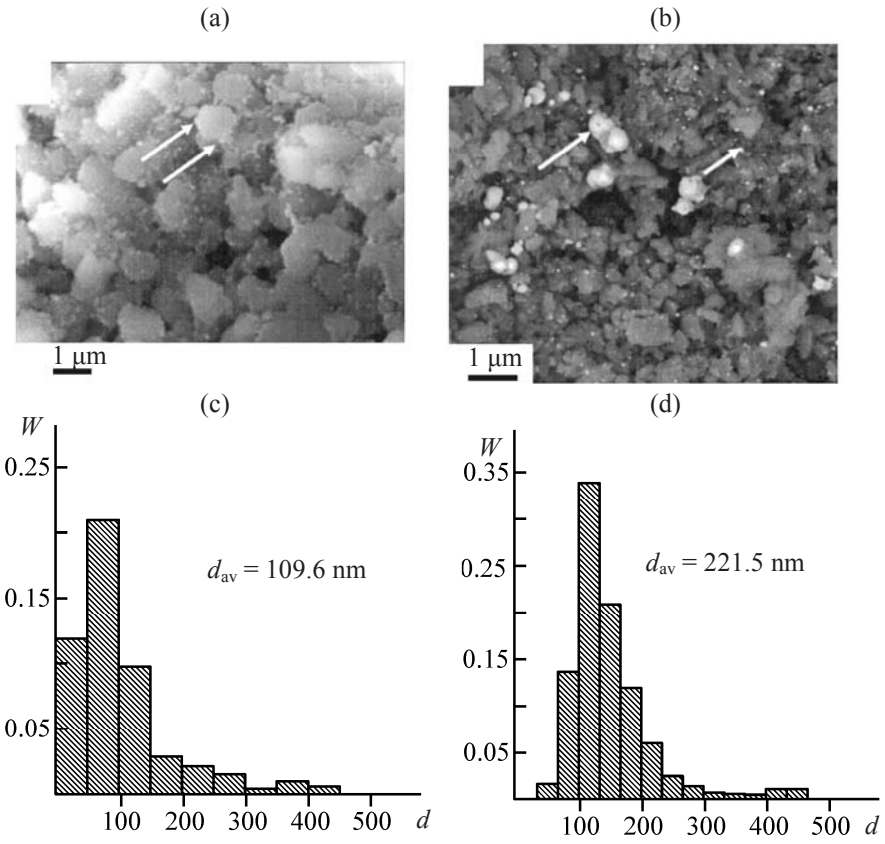


Fig. 4. (a, b) SEM images of the surface of a silver catalyst supported by granulated silicon nitride and (c, d) particle size distribution histograms (a, c) before the catalytic reaction and (b, d) after catalysis. Silver particles supported by silicon nitride are indicated by arrows.

study systems produced by fractional reduction of silver from a silver nitrate solution on the surface of Si_3N_4-I and Si_3N_4-II supports. The XPA spectra of all the silver-containing samples (Figs. 1a, 1b) contain distinct lines characteristic of α- and β-modifications of silicon nitride, as well as lines characteristic of metallic silver. The width of coherent scattering region (SCR) of silver particles in Ag/Si_3N_4-I and Ag/Si_3N_4-II samples is 30±10 nm, i.e., formation of nanosize particles is characteristic of both systems. A comparison of the intensities of the silver lines in the XPA spectra demonstrated that, for samples produced by fractional reduction on highly dispersed silicon nitride (Ag/Si_3N_4-I and Ag/Si_3N_4-II samples), silver can be deposited in the metallic state in amounts of 3.5 and 2 wt %, respectively (see table; Figs. 1a, 1b). The same content of the active component was obtained in a study of the chemical composition of the samples by the XFS method.

The XPA spectra of a silver sample supported by silicon nitride with a predominant content of the α-modification (Fig. 1a) contain principal lines of silver: (111), (200), and (220). The relative intensities of the Ag lines are in agreement with tabulated data (ASTM), which indicates that the nanoparticles formed have no texture features. The spectrum of a sample supported by Si_3N_4-II (Fig. 1b) shows only two lines of silver, (111) and (200), which have a lower intensity as compared with the Ag/Si_3N_4-I system. Thus, silver is deposited in a smaller amount onto silicon nitride of predominantly the β-modification, compared with the other sample, under identical conditions of synthesis of silver-containing systems (see table). This may be due to differences in the mechanisms of interaction between the support surface and silver particles; probably, the interaction between the surface of the β-modification of Si_3N_4 and Ag is weaker.

In addition to differences in the quantitative content of supported silver particles, Ag/Si_3N_4-I and Ag/Si_3N_4-II samples exhibit markedly different morphological features. TEM images of the samples are shown in Fig. 3, together with the corresponding size distribution

histograms of the resulting silver particles. It can be seen that both systems are characterized by the presence of nanosize silver particles. However, for the sample supported by Si_3N_4-I (predominant α-phase), the particles have a broader size distribution (56–63 nm) and their average diameter is about 22 nm (Fig. 3d). The silver particles have an elongated shape and are localized on projections (depressions) on the surface of silicon nitride crystals (Figs. 3a, 3b; Ag nanoparticles are shown by arrows). If cylindrical particles are present in the support material, silver particles are predominantly formed at places of contact between support particles, rather than on the silicon nitride surface (Fig. 3b). This mechanism of formation of supported metal particles is operative under conditions of a weak chemical interaction between the support and a component deposited [11].

Silver particles on the Ag/Si_3N_4-II sample are smaller in size and have a narrower size distribution; the average size was about 10 nm (Figs. 3c, 3e). The particles are spherical and more uniformly distributed over the support surface (Fig. 3c). However, predominant localization of silver particles is observed along edges of "whiskers" in silicon nitride.

It is known that analysis of the grain size distribution can provide information about the formation mechanism of nanoparticles [12]. If a normal particle size distribution is observed, this indicates that particles grow via addition of single atoms (condensation mechanism), whereas in the case of a logarithmically normal distribution, the coalescence mechanism prevails, by which particle grow via their combination. The logarithmically normal distribution is observed in both cases. However, the existence of a broad grain size distribution in the Ag/Si_3N_4-I sample is a prerequisite for an intense increase in the grain size at elevated temperature, because large grains in the structure are nuclei for anomalous growth via "consumption" of their smaller "fellows."

Thus, depending on the structural-phase state, morphology, and chemical composition of the support surface, silver particles differing in size and localization place are formed. The atomic microcosmposition of the surface (Si/N ratio, presence of oxygen-containing centers) varies between different silicon nitride phases [13]. Accordingly different are both the nature and arrangement of nucleation centers and the growth mechanism of silver nanoparticles.

It was of interest to analyze the possibility of formation of uniform-size silver nanoparticles on the surface of silicon nitride grains with predominant content of the β-modification (Si_3N_4-III sample) and to examine their catalytic activity in partial oxidation of ethylene glycol. The catalysts were synthesized by fractional reduction of silver nitrate with sodium borohydride and deposition of silver phosphate, followed by thermal treatment. With the FCR method used for deposition of the active component onto Si_3N_4-III grains, the support weakly interacts with the active phase, because, according to the XPA and XFS data, the amount of supported silver is less than 1% (see table, Fig. 1c). The XPA spectrum contains only one principal line of Ag, (111), which has low intensity.

As noted above for the example of dispersed silicon nitride, of particular importance for formation of nanoparticles of the active component on the support surface is the presence of edges and places of contact between adherent particles in the support material. It can be seen in surface SEM images of a silver catalyst deposited onto silicon nitride grains by fractional reduction (Fig. 4) that this synthesis method makes it possible to obtain silver on the whole support surface in the form of spherical particles 10–450 nm in size; the average particle size is about 109 nm (indicated by the arrow in Fig. 4). Despite the close phase compositions of the highly dispersed Si_3N_4-II sample and grains of the Si_3N_4-III sample, the presence of energy-uncompensated formation centers of silver particles on the Si_3N_4-III support results in the substantially smaller amount of the supported active phase, compared with the highly dispersed Ag/Si_3N_4-II sample. The broad particle size distribution and the presence of particles with sizes exceeding 200 nm (Figs. 4a, 4c) possibly indicates that the coalescence mechanism of particle growth is predominant.

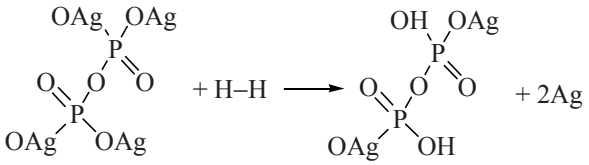
The content of the active component on the support surface in fabrication of supported catalytic systems can be raised by introduction of metal compounds whose decomposition (reduction) under the catalytic process conditions yields active centers [14]. Therefore, it was of interest to study the possibility of using silver phosphate as a precursor-compound to form particles of the active component on the silicon nitride surface. This can be done because silver phosphate is readily reduced under the action of reducing agents contained in the reaction mixture for partial ethylene glycol oxidation to give dispersed Ag particles [15].

In the case of silver phosphate deposition (Ag–P–O/Si_3N_4-III sample), the content of the active component on the support is 5.0 wt % according to XFS and XPA data (see table), which may be due to the stronger interaction of the support surface with the supported phase (Fig. 1d).

The XPA spectra in Fig. 1d contain, in addition to the principal lines of the support, bands characteristic of silver phosphate (Ag_3PO_4). The Ag–P–O/Si_3N_4-III sample of silver-containing silicon nitride, produced using silver phosphate, strongly differs in morphology from samples fabricated by the FCR method. Silver phosphate is distributed over the surface in the form of polylayer formations incompletely covering the support surface (Fig. 5a). The deposited silver phosphate layer has cracks (Fig. 5b) resulting from the macroscopic morphology of the grain surface of the Si_3N_4-III sample.

The catalytic properties of silver-containing catalysts supported by silicon nitride (Ag/Si_3N_4-III and Ag–P–O/Si_3N_4-III) were studied in the reaction of partial oxidation of ethylene glycol to glyoxal in a flow-through installation. The systems exhibit a catalytic activity comparable with that of supported Ag catalysts on aluminosilicate supports [9]. The table lists the results obtained in the study of the catalytic activity of silver-containing catalysts at $EG/O_2 = 1.2$. As temperature is raised from 500 to 600°C, the conversion of ethylene glycol increases from 72 to 93–95%. The selectivity shows a maximum at 530°C and is 50% for the Ag/Si_3N_4-III sample and 24% for the Ag–P–O/Si_3N_4-III catalyst.

Noteworthy is the fact that the catalytic reaction medium strongly affects the morphology of silver-containing systems (Figs. 4c, 4d; 5c, 5d). On using the samples under study in catalysis, the content of the active component decreases and Ag particles undergo agglomeration under the reaction conditions. As follows from Fig. 5c, separate highly dispersed silver particles and coarse Ag agglomerates up to 650 nm in size appear on the support surface, instead of silver phosphate layers, upon treatment under the catalytic process conditions. The absence of silver phosphate is due to the reduction of the metal in its interaction with hydrogen by the reaction



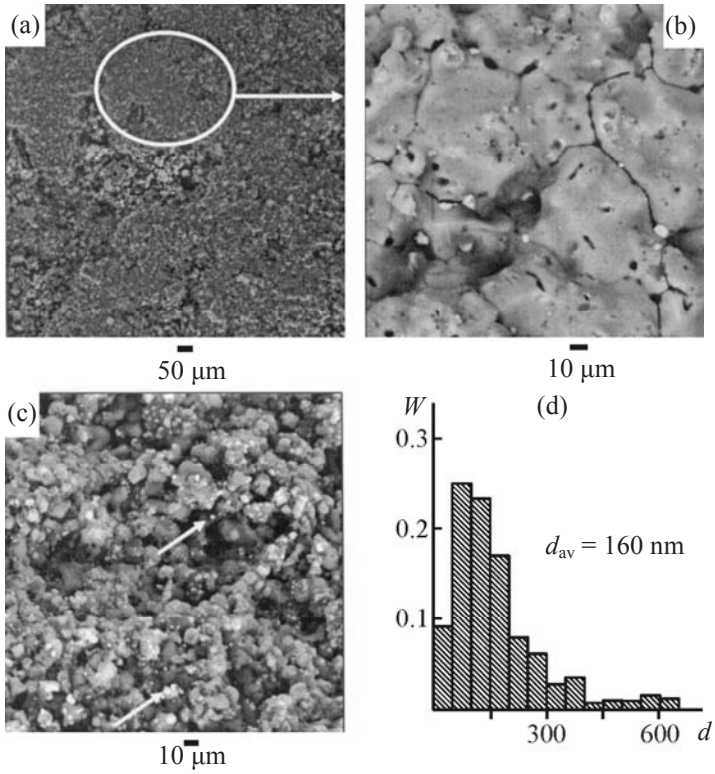


Fig. 5. SEM images of a phosphorus-containing silver catalyst Ag_3PO_4/Si_3N_4-III (a, b) before the catalytic reaction and (c) after catalysis. (d) Size distribution histogram of silver particles after catalysis.

The reduction of copper and silver phosphates to give metal particles under the action of the reaction mixture used in glyoxal synthesis has been found previously in analysis of the formation mechanisms of the active surface of polycrystalline Cu and Ag catalysts in the presence of phosphates [16]. The formation of coarse silver agglomerates on the surface of the Ag–P–O/Si_3N_4-III samples may be due to the carryover of the polyphosphate component by the flow of the reaction mixture. The desorption and carryover of the polyphosphate occur because chemical bonds providing a rather firm fixation of the polyphosphate on the support are not formed between the surface of the silicon nitride support and the polyphosphate.

Thus, despite the substantially higher content of the active component in the Ag–P–O/Si_3N_4-III sample as compared with the Ag/Si_3N_4-III sample fabricated by the FCR method, the maximum selectivity toward glyoxal was achieved for the latter sample (see table). The morphological data presented here suggest that highly dispersed silver particles less than 100 nm in size are responsible for the selective formation of glyoxal and these systems may be promising catalysts for partial oxidation of ethylene glycol into glyoxal.

CONCLUSIONS

(1) Samples of silver particle supports with different dispersities (powder, grains), phase compositions (α/β ratio), and particle morphologies (whiskers, columnar crystals, shapeless formations) were obtained, depending on the silicon nitride synthesis conditions.

(2) If a highly dispersed silicon nitride is used, nanosize metallic particles are formed (10–22 nm). However, the amount of supported silver strongly depends on the α/β phase ratio. The strongest interaction of the highly dispersed support with the active silver phase is observed when a material predominantly containing the α-modification is used, whereas silver particles on the a support with β-modification are spherical and more uniformly distributed over the support area.

(3) Silver deposited by fractional precipitation onto the surface of silicon nitride grains has the form of spherical uniformly distributed particles 109 nm in size, and that produced by the phosphate method is deposited as silver phosphate polylayers. If silicon nitride is used in the form of grains, silver deposited by the fractional precipitation method is produced with a significant loss. Under the conditions of the catalytic reaction, the content of the active component decreases and silver particles undergo agglomeration.

(4) Silver-containing systems formed by deposition onto granulated silicon nitride exhibit fairly high activity and selectivity toward glyoxal and are promising for fabrication of catalytic composites on their basis.

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