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> INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Relationships in Formation of Silicon Nitride-Supported Metal Nanoparticles

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Abstract—The state of the particles of silicon nitride-supported metal (platinum, palladium, silver) depending on the support preparation conditions and the active component loading technique was examined in relation to the structural features and phase composition of the support. The common and different features in formation of the metal nanoparticles on the silicon nitride surface were identified.

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An essential prerequisite for transition to advanced technologies consists in development of novel materials whose functional characteristics are determined by the properties of the specially created microareas, as well as by the processes occurring at the atomic and molecular levels in monolayers and nanobulks. One of the major challenges faced by nanotechnology researchers is stabilization of nonequilibrium nanoparticles without major loss of their high reactivity. In this context, a topical task consists in directed synthesis of stable and active metallic nanoobjects whose high functional activity is preserved in catalytic processes, especially at high temperatures. This challenge is typically solved via the use of various stabilizing matrix supports. However, this route is associated with certain complications, e.g., agglomeration of the particles and entrainment of the active phase, which hinder further use of these materials as catalytically active systems. Moreover, under expo-sure of the nanosystems to increased temperatures and/or redox reactant mixtures, weak interaction of nanoparticles with the support surface may lead to the loss of the functional properties by the nanoheterogeneous system. At the same time, the physicochemical and functional properties of the nanoparticles involved in the chemical reaction may be affected not only by the particle size but also by

the nature of the matrix support and reaction medium. In this context, there is an urgent need to develop approaches to preserving high reactivity of the nanoparticles stabilized by support matrices so as to make them suitable as active components of catalytic systems in specific processes.

For metal (in particular Pd, Pt, and Ag) particles, exhibiting catalytic activity in high-temperature processes (deep oxidation of hydrocarbons, hydrogenation of carbon monoxide, partial oxidation of alcohols, etc.), suitable supports are conventionally found in oxide systems: silica, alumina, aluminosilicates [1]. However, such systems often lose their activity via agglomeration and entrainment of the active phase. Prolonged activity of nanoparticles under high-temperature redox reaction conditions can be achieved with an alternative support, silicon nitride. It possesses high thermal conductivity, as well as high strength and corrosion resistance and low oxidation rate, which properties are of prime importance for high-temperature exothermic catalytic processes (deep oxidation of methane, partial oxidation of ethylene glycol to glyoxal) [2].

All the basic principles of preparation of supported metal systems, described in literature, concern oxide supports. Interaction of platinum/palladium/silver complexes with the oxide (Al₂O₃ and SiO₂) surface, associated with metal–support bonding, were studied in detail, while data on formation of Pt, Pd, and Ag particles on non-oxide supports are scarce. The approaches practiced in synthesis on oxide systems are not absolutely applicable to the preparation of ceramicsupported systems. Of key importance for the catalytic properties of metal nanoparticles, along with the nature of the support, will be the deposition conditions (chemical nature of the precursor of the particles, polarity of the medium, nature of the solvent, and heat treatment conditions).

Here, we examined the state of the supported metal particles (platinum, palladium, silver) in relation to the structural features, phase composition of silicon nitride, and active component loading technique. Also, we tested the prepared materials as candidate catalysts for selective and deep oxidation of organic substances.

EXPERIMENTAL

We used silicon nitride samples with different specific surface areas and phase compositions (Table 1): commercially available crystalline materials (Si₃N₄-I, Si₃N₄-II) and samples prepared by self-propagating high-temperature synthesis technique [3–5] (Si₃N₄-III). Also, we used silicon nitride samples comprising amorphous fraction, Si₃N₄-am. This material contained ~20 wt% crystalline fraction of silicon nitride with the α/β phase ratio of ~2.3. The Si₃N₄-cal support was amorphous silicon nitride calcined in a nitrogen atmosphere at 1400°C for 2 h, comprising amorphous fraction (up to 20 wt%) with the α/β phase ratio of up to 6.6 (Table 1) [6].

The platinum catalysts were prepared by impregnating the Si_3N_4 -I support with the appropriate

 Table 1. Main characteristics of the silicon nitride support for metal particles

Support	$S_{\rm sp},$ m ² g ⁻¹	Average size of support particles	Content of α - and β -silicon nitride phases, %		
Si ₃ N ₄ -I	6	1 μm	α 85, β 15		
Si ₃ N ₄ -II	2	1 μm	β 86, α13, Si 1		
Si_3N_4 -am	66	1 μm	Amorph. > 80 , $\alpha/\beta \sim 2.3$		
Si ₃ N ₄ -cal	28	1 μm	Amorph. < 20, $\alpha/\beta \sim 6.6$		
Si ₃ N ₄ -III	2	0.5–1 mm	β 85, α 15		

amount of Pt(II) bis-acetylacetonate dissolved in toluene. We examined (0.12 wt% Pt)/Si₃N₄-I, (0.55 wt% Pt)/Si₃N₄-I, and (0.87 wt% Pt)/Si₃N₄-I samples. The notations for the platinum systems include the initial amounts of the metal on the support [7]. The systems with close palladium loadings (~0.5 wt%) were prepared by impregnating the supports with a solution of Pd bis-acetylacetonate in toluene (samples Pd/ Si_3N_4 -I, Pd/ Si_3N_4 -II, Pd/ Si_3N_4 -am, Pd/ Si_3N_4 -cal) [6, 8, 9]. To elucidate the influence of the nature of the solution, we prepared two catalysts by impregnating silicon nitride (Si_3N_4-I) with a solution of Pd(II) acetate in toluene (Pd/Si₃N₄-I-t) and water (Pd/Si₃N₄-I-w). Upon interaction of the supports with solutions of palladium or platinum salts and drying at 80°C the samples were exposed to an argon stream for 2 h at 500°C, subsequently at 350°C for 2 h to an oxygen stream, and finally to a hydrogen stream at 500°C for 2 h [8]. The content of the active component (palladium, platinum) on the support was determined on an ICP atomic emission spectrometer accurately to within 2%.

The support for silver catalysts was found in the Si₃N₄-III sample. The active component was deposited onto the silicon nitride surface (as calculated for 5 wt%) by two methods: (1) fractional deposition including vigorously stirring of the silver nitrate solution with the support, silver reduction with sodium tetraborohydride, and 20-h settling of the resulting mixture, followed by centrifugation and calcination of silicon nitride with the reduced silver in an O_2 stream at 400°C (Ag/Si₃N₄-III-FR sample) and (2) impregnation from an organic medium, including preparation of silver trifluoroacetate crystals, dissolution of silver trifluoroacetate in toluene, impregnation of the support with the resulting solution for 2 h, evaporation of toluene, and sequential calcination at a rate of 1 deg min-1 to 500°C in an oxygen stream (Ag/Si₃N₄-III-OI sample). The content of the active component (silver) on the support surface was monitored by X-ray fluorescence spectroscopy (XFS) on a Quant'X (XFS) spectrometer.

The catalytic performance of the palladium and platinum systems in deep oxidation of methane were examined in a continuous quartz reactor at temperatures within 25–650°C in two modes: (1) on freshly prepared samples at linearly increased temperature (3 deg min⁻¹) and (2) on catalysts, preliminarily exposed to the reaction mixture for 3 h at 650°C (temperature increase

at a rate of 1 deg min⁻¹). In our experiments we used the $CH_4/O_2/N_2$ reaction mixture with the percent ratio of 2.5/19.5/78 at the feeding rate of 100 ml min⁻¹. The composition of the reactants at the reactor outlet was monitored by mass spectrometry.

The catalytic activity of the synthesized silver systems was tested for partial oxidation of ethylene glycol (EG) to glyoxal (GO) using a continuous fixed-bed catalytic setup (inner diameter of the reactor 16 mm) [10]. The catalyst bed height was 20 mm; the reaction mixture had the molar composition $(CH_2OH)_2/H_2O/O_2/N_2 = 1.0/3.4/1.0/10.0$, and the contact time was 0.06 s. The catalytic activity was determined at temperature varied within 500–620°C.

The elemental composition of the catalyst surface and electronic properties of platinum and palladium before and after deep oxidation of methane were



Fig. 1. TEM images of Pt/Si_3N_4 -I catalysts (a, c, e) before and (b, d, f) after deep oxidation of methane.



Fig. 2. XPS data for catalysts with different Pt loadings. (*I*) Intensity and (E_b) binding energy, eV. (a) Evolution of the Pt4f spectra, (b) [Pt4f]/[Si2p] ratio, and (c) Pt content, at.%, on the catalyst surface. (*I*) Before and (*2*) after the reaction.

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Platinum loading, wt % ^a		Pt4 $f_{7/2}$ binding energy, eV ^a		[Pt4 <i>f</i>]/[Si2 <i>p</i>]		Average particle size, nm	
BR	AR	BR	AR	BR	AR	BR	AR
0.12	0.12	72.05	71.1	0.008	0.003	2	11
0.55	0.52	71.4	71.1	0.026	0.007	3	11
0.87	0.83	71.4	71.1	0.032	0.012	6	16

Table 2. Surface properties of silicon nitride-supported platinum catalysts Pt/Si₃N₄-I

^a BR and AR refer to the catalysts before and after deep oxidation of methane, respectively.

determined by X-ray photoelectron spectroscopy (XPS) on an ESCALAB 200R spectrometer with $Mg_{K\alpha}$ radiation (hv = 1253.6 eV). The charging effect during photoemission was taken into account using the internal reference method, based on the N1s spectrum of the support with the binding energy $E_{\rm b} = 397.6$ eV. The phase composition and structural parameters of the catalyst samples were determined by X-ray phase analysis (XPA) on an XRD-6000 diffractometer using $Cu_{K\alpha}$ radiation. The relative content of the phases in silicon nitride was estimated from the relative intensities of the corresponding lines in the diffraction patterns [8]. The structural features of the support and the catalysts were examined by raster electron microscopy (REM) on SEM 515 Philips and Tescan LMU II instruments, as well as by transmission electron microscopy (TEM) on a Philips CM 30 instrument.

The reaction of oxygen with the Si_3N_4 -I support and palladium catalyst surfaces was studied by temperatureprogrammed desorption (TPD) of oxygen. Before the TPD experiments the samples were exposed to a helium stream at temperatures within 25–900°C for 6 h. The TPD spectra were recorded for the samples exposed to an oxygen stream (feed rate 100 ml min⁻¹) by the following scheme: T = 25°C, 5 min; T = 200°C, 5 min; T = 800°C, 1 h. The TPD spectra were taken in a helium stream (100 ml min⁻¹) within 25–800°C at the heating rate of 5 deg min⁻¹; the desorbed gases were analyzed by mass spectrometry.

The CO adsorption on the catalyst surface was studied by IR spectroscopy on a Bruker FTIR-22 V spectrometer. The IR spectra were measured within 4000–400 cm⁻¹ at 1 cm⁻¹ resolution. Before adsorption the samples were heated at 433 K for 4 h. The CO adsorption was carried out at 25°C for 40 min. After recording the spectra of the adsorbed species at the adsorption temperature the samples were heated under evacuation and kept at the appropriate desorption temperature for 40 min. The spectrum was recorded for the samples cooled to room temperature, after which the above-described procedure



Fig. 3. Deep oxidation of methane on Pt/Si₃N₄-I catalysts: (a) temperature corresponding to 50% conversion T_{50} , °C, for (1) freshly prepared systems and (2) systems exposed to the reaction mixture and (b) variation of the methane conversion φ , %, with temperature T, °C, for the catalysts exposed to the reaction mixture. The Pt content, wt%: (1) 0.12, (2) 0.55, and (3) 0.87.

was repeated at a higher temperature. The experimental results are represented by a series of the IR spectra of the adsorbed CO layers at different desorption temperatures (T 100, 200, 300°C).

Silicon Nitride-Supported Platinum-Containing Systems. Table 2 summarizes the main physicochemical properties of the surface of the platinum catalysts prepared. Chemical analysis showed that, for the freshly prepared samples, 0.12, 0.55, and 0.87 wt% platinum was supported on silicon nitride. The TEM examinations of Pt/Si₃N₄-I revealed the presence of nanocrystalline Pt particles on the surface of the freshly prepared systems (Fig. 1). The (0.12 wt% Pt)/Si₃N₄-I sample was characterized by the average particle size of 2 nm (Table 2, Fig. 1a). The metal particles for the remaining catalysts were slightly larger: The average particle size for the (0.55 wt% Pt)/Si₃N₄-I sample was 3 (Table 2, Fig. 1c), and that for (0.87 wt% Pt)/Si₃N₄-I, 6 nm (Table 2, Fig. 1e), respectively.

Figure 2a shows the Pt4*f* core-level XPS spectra of the Pt-containing systems examined. It is seen that, before catalysis, the Pt4*f* XPS line grows in intensity with increasing amount of the supported platinum, thereby increasing the [Pt4*f*]/[Si2*p*] line ratio (Table 2; Figs. 2a and 2b). The binding energy for the (0.12 wt% Pt)/Si₃N₄ sample exceeded that for bulk platinum metal (72.05 against 71.2 eV) (Fig. 2a). At the same time, the position of the Pt4*f*_{7/2} lines (E_b = 71.4 eV) for (0.55 wt% Pt)/Si₃N₄ and (0.87 wt% Pt)/Si₃N₄ is very close to that of the metallic state and exceeds the binding energy of the latter by 0.2 eV only (Fig. 2). The observed shift of the Pt4 $f_{7/2}$ line is smaller than that recorded in oxidation of platinum (> 1 eV), which suggests the metallic nature of the supported particles. Such increase in binding energy is characteristic for heterogeneous catalysts containing metal nanoparticles on the support surface, especially those with a size of 2–5 nm. The observed effect is associated either with a slight deficiency of electron density on the metal crystallites, resulted from strong interaction of the supported metal nanoparticles with support surface segments, or with relaxation of the hole yielded by photoemission (final-state effect) [11].

The synthesized platinum catalysts were tested in deep oxidation of methane. Figure 3 shows how the methane conversion varies with increasing temperature for the freshly prepared samples and for the systems that were preliminarily exposed to the reaction mixture at 650°C for 3 h. It is seen that (0.12 wt% Pt)/Si₃N₄-I sample is characterized by a low activity: Exhaustive conversion of methane was not achieved up to 650°C, and 50% conversion was observed only at 610°C (Fig. 3a). The catalysts containing 0.55 and 0.87 wt% Pt afford higher methane conversions than the sample with the lowest metal loading (Fig. 3a). For (0.55 wt% Pt)/Si₃N₄-I and (0.87 wt% Pt)/Si₃N₄-I the 50% conversion of methane was achieved at 478 and 468°C, respectively. However, the activity of all the three systems decreases upon exposure to the reaction mixture. For the



Fig. 4. Conversion φ , %, of methane on the silicon nitride-supported palladium catalysts vs. temperature *T*, °C. (a) Freshly prepared systems and (b) samples preliminarily exposed to the reaction mixture for 3 h at 650°C. (*1*) Pd/Si₃N₄-I, (*2*) Pd/Si₃N₄-cal, (*3*) Pd/Si₃N₄-am, and (*4*) Pd/Si₃N₄-II.

 $(0.12 \text{ wt\% Pt})/\text{Si}_3\text{N}_4$ catalyst the 50% methane conversion was achieved at 615°C only, and for the samples with a higher metal loading, at 550–560°C (Fig. 3b).

To explain the observed deactivation, we examined the surface properties of the platinum catalysts upon deep oxidation of methane. Chemical analysis showed (Table 2) that, for the sample with the lowest metal loading, the amount of the deposited platinum remains unchanged after catalysis (0.12 wt% Pt). For the remaining two catalysts, it slightly decreased to 0.52 and 0.83 wt%, respectively (Table 2). This is due to entrainment of the metallic phase (in the amount of no greater than 5%) with the reaction products from the support surface.

The TEM data suggest that, during the catalytic reaction, the metal particles on the samples surface were agglomerated into crystallites whose size strongly exceeded that for the freshly prepared systems. This is clear from the TEM images shown in Figs. 1b, 1d, and 1f. On the surface of the (0.12 wt% Pt)/Si₃N₄-I catalyst there were particles with sizes up to 30 nm (Table 2). At the same time, the crystallites for the remaining samples measured up to 70 nm (average size 11 and 16 nm, respectively; Table 2).

An XPS examination of the Pt/Si₃N₄ samples after methane oxidation showed that the platinum particles were not oxidized during the catalysis. After the reaction all the catalysts were characterized by the Pt4 $f_{7/2}$ binding energy of 71.1 eV, which is close to $E_{\rm b}$ for the bulk platinum metal (Table 2, Fig. 2). However, Table 2 shows that the [Pt4f]/[Si2p] ratio decreases due to a decrease in intensity of the Pt4f peaks (Fig. 2a). The most pronounced decrease was observed for the sample with the maximal platinum loading, $(0.87 \text{ wt}\% \text{ Pt})/\text{Si}_3\text{N}_4$. These changes in the Pt4f XPS signal and [Pt4f]/[Si2p] ratio relative to the initial state may be associated with entrainment of platinum and/or agglomeration of the metal particles during the catalytic reaction. It should be noted that both factors apply to the case of catalysts with the maximum and medium platinum loadings. At the same time, for the (0.12 wt% Pt)/Si₃N₄ sample a decrease in the [Pt4f]/[Si2p] ratio is associated with agglomeration of the metal particles on the support surface solely.

Agglomeration, like entrainment of the metal under catalytic oxidation conditions, is also known for other platinum catalysts [12–14]. A decrease in the [Pt4*f*]/[Si2*p*] ratio, associated with the Pt loss, was



Fig. 5. TEM images of the silicon nitride-supported palladium particles: (a) Pd/Si_3N_4 -I sample before the catalytic reaction; (b) palladium particles supported on Si_3N_4 -II (β -phase) after deep oxidation of methane; and (c) Pd/Si_3N_4 -am after the catalytic reaction.

revealed for silicon nitride-supported catalysts with 0.045, 1, and 2.2 wt% Pt in high-temperatures selective oxidation of methane [15]. Presumably, at high temperatures, silicon nitride-supported platinum catalysts can be involved in two processes under the reaction conditions: sintering (agglomeration)



Fig. 6. TPD spectra of O_2 from palladium-containing catalysts in relation to the sample–oxygen interaction temperature *T*, °C. (*D*) O_2 desorption, arb. units. (a) Adsorption at 25°C and (b) oxidation at 800°C. (*1*) Pd/Si₃N₄-I-a and (*2*) Pd/Si₃N₄-I-t; the same for Fig. 7.

Table 3. Silicon nitride-supported palladium catalysts

of nanosized metal particles into large particles and oxidation of large particles to PtO_x , followed by sublimation at high temperature [5, 11–14].

Silicon Nitride-Supported Palladium-Containing Systems. Table 3 summarizes the main characteristics of the palladium-containing catalysts examined. The technique proposed for palladium particle preparation allows formation of the Pd nanoparticles on the silicon nitride surface. Catalytic examinations showed that the Pd/Si₃N₄-I sample was active and stable both in the initial state and after 3-h exposure to the reaction mixture. The 50% conversion of methane was achieved at 360°C, and exhaustive conversion, at 400°C (Table 3, Fig. 4). By contrast, the palladium catalyst supported on Si₃N₄-II (with β -phase dominating) was completely deactivated during the reaction, and exhaustive conversion of methane was not achieved throughout the temperature range examined. Comparison of the catalytic properties of the palladium catalysts supported on silicon nitride comprising an amorphous fraction showed the following. The half conversion of methane was achieved with Pd/ Si₃N₄-am and Pd/Si₃N₄-cal samples at 430 and 370°C, respectively, which temperatures are comparable with that for Pd/Si₃N₄-I. However, upon exposure to the reaction mixture the catalytic activity decreased for both systems.

The difference in the catalytic properties is not

Sample	Metal particle precursor	Pd loading, wt%	Pd3p _{5/2} binding energy, eV		Average size of Pd particles, nm		Temperature corresponding to 50% conversion of CH_4 , °C	
			BR	AR	BR	AR	Ia	IIa
Pd/Si ₃ N ₄ -I	$Pd(C_5H_70_2)_2,$ toluene	0.49	335.9	337.3	4.3	5.8	360	360
Pd/Si ₃ N ₄ -II	$Pd(C_5H_70_2)_2,$ toluene	0.42	335.8	337.0	5.6	5.7	480	_
Pd/SiN-am	$Pd(C_5H_70_2)_2,$ toluene	0.43	335.3	337.1	2.9	3.2	430	530
Pd/SiN-cal	$Pd(C_5H_70_2)_2$, toluene	0.45	335.9	337.3	3.2	3.6	370	470
Pd/Si ₃ N ₄ -I-t	Pd(CH ₃ C0 ₂) ₂ , toluene	0.58	335.5	337.3	4.3	4.8	307	317
Pd/Si ₃ N ₄ -I-w	Pd(CH ₃ C0 ₂) ₂ , water	0.53	335.8	337.4	49	8.3	427	602

^a I and II refer to the freshly prepared samples and those preliminarily exposed to the reaction mixture for 3 h at 650°C, respectively.

associated with agglomeration of the particles and/or oxidation of palladium clusters; the binding energies for all the systems upon the catalytic reaction were close to that for the oxidized state of palladium (PdO) (Table 3). However, the TEM examinations of the Pd/Si₃N₄-II, Pd/Si₃N₄-am, and Pd/Si₃N₄-cal samples after the catalytic reaction revealed formation of amorphous SiO_r on the metal particle surface, which is due to oxidation of the β -phase of silicon nitride and the presence of amorphous fraction (Figs. 5b and 5c). The "encapsulation" of the palladium particles by the amorphous layer under catalytic reaction conditions is responsible for a decrease in the activity of the metal particles [8, 9]. Enhanced activity and stability of palladium supported on crystalline Si_3N_4 -I (α -Si_3N_4) can be associated with modification of the electronic properties of Pd-x particles via specific interaction of the active phase with α -phase of silicon nitride. The Pd3 $p_{5/2}$ binding energy for the Pd/Si₃N₄-I catalyst significantly exceeds that for other systems examined and the Pdmetal catalyst (335.3 eV) [9]. Thus, examination of the physicochemical properties of the palladiumcontaining systems supported on silicon nitride samples with different phase compositions and characteristics showed the following. The most active and stable in deep oxidation of methane is the catalyst supported on silicon nitride dominated by α -phase. An increase in the proportion of amorphous fraction and β -phase leads to deactivation of the catalyst. The resulting particles are both active and stable; they measure 5 nm, on the average (Fig. 5a).

The catalytic properties of the palladium-containing systems are also affected by the chemical nature of the precursors of reactive sites as well as by the preparation conditions. In this connection, we examined the physicochemical properties of the palladium-containing systems supported on α -Si₃N₄ (Si₃N₄-I) in relation to their preparation technique. In the course of deep oxidation of methane we examined the physicochemical and catalytic properties of the silicon nitride-supported palladium catalysts with the use of aqueous (Pd/Si₃N₄-I-a) and toluene (Pd/Si₃N₄-I-t) solutions of palladium acetate.

We showed that, all other conditions being the same, the catalytic properties of the palladium systems prepared with the use of aqueous and organic solutions of Pd acetate are different. The Pd/Si_3N_4 -I-t sample is highly active and stable. For example, with the freshly



Fig. 7. IR spectra of CO adsorbed at 25° C on the surface of palladium catalysts, recorded at different desorption temperatures. (*A*) Adsorption, arb. units, and (v) wavenumber.

prepared catalyst and the sample exposed to the reaction mixture, half conversion of methane was achieved at $307-317^{\circ}$ C (Table 3), and exhaustive conversion, at 377° C. The catalyst prepared with the use of an aqueous solution was less active toward deep oxidation of methane. For the freshly prepared Pd/Si₃N₄-I-a sample the 50% conversion of CH₄ was achieved at 427°C only (Table 3), and exhaustive conversion, at 650°C. Upon exposure to the reaction mixture the activity of the Pd/ Si₃N₄-w catalyst was significantly decreased (50% conversion at 602°C).

As follows from chemical analysis, TEM, and XPS data, Pd/Si_3N_4 -t and Pd/Si_3N_4 -w catalysts are characterized by identical active phase loadings (0.58–0.53 wt%), average particle sizes (5–9 nm), and valence states of the Pd particles, which factors do not govern the catalytic properties of the palladium-containing systems. The differences in the activities of the Pd-containing catalysts can be manifested in the stage of surface interaction of the reactants and in the adsorption and oxidation properties of Pd.

The interaction of oxygen with the support and palladium-containing system surfaces was examined by the O_2 TPD technique (Fig. 6). On the surface of neat support oxygen was adsorbed as a weakly bound, presumably molecular, species which was exhaustively

desorbed at 60°C. The TPD spectra of oxygen from supported palladium catalysts contain three peaks: a broadened desorption peak with $T_{\text{max}} = 90^{\circ}$ C and two high-temperature peaks [T_{max} (Pd/Si₃N₄-I-w) 630, 690°C and T_{max} (Pd/Si₃N₄-I-t) 700, 760°C].

Compared to neat support, the catalysts exhibit an increase in the low-temperature peak area $(T_{\text{max}} = 90^{\circ}\text{C})$ in the spectra. This is associated with superposition of the desorption peaks of weakly bound oxygen from the support and the palladium particle surfaces (Fig. 6). It should be noted that the low-temperature peak of the Pd/Si₃N₄-t catalyst has a larger area than does Pd/ Si_3N_4 -w. This is due to the presence of the reactive sites characterized by higher adsorbate-adsorbent interaction energy. The shapes and positions of the maxima for the high-temperature desorption peaks of oxygen are determined by the preparation conditions for the palladium-containing catalysts. For the Pd/Si₃N₄-I-w sample we observed a proportional growth of the thermal desorption peak areas at $T_{\text{max}} = 630$ and 690° C with increasing temperature of oxygen exposure. At the same time, for the Pd/Si₃N₄-I-t sample the desorption peaks are shifted to higher temperatures (T_{max} 700 and 760°C), and an increase in the temperature of the catalyst-oxygen interaction is accompanied by that in the areas of the TPD peaks, with the peak at $T_{\text{max}} =$ 760°C dominating. The high-temperature peaks in the TPD spectra of the catalysts are associated with diffusion and subsequent desorption of oxygen from the crystal lattice of the metal oxide (PdO_r) which is thermodynamically unstable above 680°C [16, 17]. The appearance of several thermal desorption peaks may be associated with formation of a variety of palladium oxide phases or an oxide-metal mixture with different oxygen-metal binding energies.

To examine the adsorption properties and structural characteristics of the silicon nitride-supported palladium particles, we studied the CO adsorption by IR spectroscopy. The resulting spectra (Fig. 7) contain





Fig. 8. REM images of the surface of the silver catalyst supported on granulated silicon nitride (Ag/Si₃N₄-III-OI). (a) Before catalysis and (b) corresponding particle size distribution d, nm.

an absorption band near 2075 cm⁻¹ and that at 2000– 1800 cm⁻¹, comprising three components (1972, 1914, 1829 cm⁻¹). As known [16], bands above 2000 cm⁻¹ are characteristic for adsorption of linear CO molecules, while the adsorption of bridged CO molecules is manifested below 2000 cm⁻¹. Weaker, compared to high-coordination sites, bonding for low-coordination

Sample	Particle size, nm		Ag conte	ent, wt%	Catalytic properties ^a	
_	BR	AR	BR	AR	K _{EG} , mol%	S _{GO} mol%
Ag/Si ₃ N ₄ -III-DV	109	222	0.45	0.15	97.8	23.8
Ag/Si ₃ N ₄ -III-PO	83	94	5	5	80.9	45.6

Table 4. Characteristics of the silicon nitride-supported silver catalysts

 a K_{EG} is conversion of ethylene glycol, and S_{GO}, selectivity with respect to glyoxal.

sites is manifested at higher frequencies [16]. The band at 2075 cm⁻¹ is associated with adsorption of linear CO molecules in the Pd(111) plane, and those at 1914 and 1829 cm⁻¹, with adsorption of bridged CO in (111) plane interstices [18]. The band at 1972 cm⁻¹ belongs to bridged CO molecules in the (100) plane and the molecules adsorbed on the defect edges and steps of metal clusters that mainly contribute to this band [18, 19].

The intensity of the IR bands is determined by the preparation conditions for the palladium systems. By contrast to Pd/Si₃N₄-I-w, the Pd/Si₃N₄-I-t catalyst is characterized by the highest intensities of all the bands in the IR spectra (Fig. 7). With increasing desorption temperature for Pd/Si₃N₄-I-t, the absorption bands at 2075 and 1972 cm⁻¹ disappear above all, and at the desorption temperature of 200°C the spectrum contains only the IR bands at 1914 and 1829 cm⁻¹. The peaks associated with CO adsorption completely disappear at 300°C. For Pd/Si₃N₄-I-w catalyst all the IR bands tend to decrease in intensity proportionally to increasing desorption temperature and completely disappear at 200°C. The IR-spectroscopic data we obtained suggest that the Pd/Si₃N₄-I-t catalyst, active in methane oxidation, comprises palladium clusters with the Pd(111) orientation dominating, and the CO adsorption sites are characterized by higher interaction energies.

Thus, the TPD and IR examinations of the palladium systems showed that the Pd/Si₃N₄-I-t and Pd/Si₃N₄-I-w catalysts significantly differ in the structure and adsorption properties of the nanoparticles. This affects the adsorption forms of reactants, as well as the oxidative properties and mechanism of the surface reactions. The structure and physicochemical properties of the active sites on the surface of the particles formed under the preparation conditions are directly affected by the structure of the palladium complexes adsorbed on the support during preparation, as well as by the atomic composition and acid-base properties of the support surface. This suggests the key importance of the nature of the solvent in formation of palladium particles active in deep oxidation of methane. The presence of water may affect the decomposition of the palladium complexes on the support surface, and the Pd yielded by reduction exhibits a comparatively low catalytic activity. Also, the solvent can strongly modify the surface characteristics of the support.

Silicon nitride-Supported silver-containing

Systems. Table 4 presents the characteristics of the silicon nitride-supported silver systems. The X-ray phase analysis and XFS examination revealed weak interaction between the support and the active phase: The amount of the actually deposited supported silver was <1% against 5% as calculated before deposition (Table 4). Synthesis of Ag/Si₃N₄-III-FR catalyst by fractional reduction allows formation of silver throughout the surface of the support in the form of 11-480-nm particles with the average size of 109 nm. Notably, these particles are localized on chips, edges, and protruding faces of the support. Like with dispersed silicon nitride [20], of much significance for formation of the active component nanoparticles on the support surface are the edges and the contact sites between the intergrown particles in the support material, i.e., energyuncompensated sites of metal particle formation.

Figure 8a shows the REM image of the surface of the sample prepared by deposition of silver trifluoroacatate from a toluene solution (Ag/Si₃N₄-III-OI). It is seen that the active component particles are uniformly distributed over the support surface, with the particle size of ~83 nm dominating. For the majority of the particles, the size ranges form 23 to 400 nm (Fig. 8a). It should be noted that the particle size distribution (Fig. 8b) is narrower than that for the catalyst prepared from aqueous medium. This fact suggests a uniform size of the resulting particles. Importantly, under these preparation conditions there was no loss of the active component. By contrast to aqueous solution of the silver particle precursor, an organic solvent affords exhaustive deposition of silver (5 wt%, Table 4).

We examined the catalytic properties of the prepared silver systems in relation to the oxygen content in the reaction mixture for O_2/EG ratios within 0.8–1.3 at 580 and 560°C. Also, we studied the catalytic behavior of the systems at 530–600°C for the O_2/EG ratio of 1.2. We found (Table 4) that the Ag/Si₃N₄-III sample prepared from toluene is the most active among the catalysts examined. The selectivity with respect to GO throughout the O_2/EG ratio range examined was 45–50%, the EG conversion being 80–81%.

The catalytic activity of the system prepared by us is comparable with that of aluminosilicate-supported silver catalysts [10, 21]. The supported Ag catalysts are slightly superseded in catalytic activity by polycrystalline silver which is conventionally used as catalyst for synthesis of glyoxal by catalytic oxidation of ethylene glycol [21]

(conversion 95–100 against ~90% and selectivity with respect to glyoxal, 45–55 against 55–65%). However, supported catalysts offer major advantages over bulk analogs in terms of enhanced sintering resistance of the active surface under high-temperature conditions, less carbon deposition, etc. Owing to the unique properties of silicon nitride (in particular, high thermal conductivity) utilized in the catalytic systems prepared by us, is it possible to synthesize glyoxal over a broader, compared to other supported Ag catalysts, temperature range (up to 650°C) without significant loss of selectivity with respect to the target product and without formation of carbon deposition products.

To explain the difference in the catalytic properties of the systems prepared from aqueous and organic media, we examined their morphological properties after the catalytic processes. On the Ag/Si₃N₄-III-FR surface there were particles with the average size of 222 nm, nonuniformly distributed over support surface. Comparison of the morphologies of the samples before and after the catalysis revealed agglomeration of the active phase, accompanied by a twofold increase in the average particle size. On the support surface there were agglomerates with the size of up to 2 µm, formed from smaller particles occurring in close proximity to one another under the reaction conditions. The XFS examination showed that, in the sample prepared from aqueous solution, agglomeration is paralleled by major entrainment (up to 70%) of catalytically active phase; after catalysis the amount of the active component was 0.15 wt% (Table 4).

In the case of Ag/Si₃N₄-III-OI sample prepared from organic medium we did not reveal any significant changes in morphology. The average particle size was 94 nm. Also, there were a small number of agglomerates ranging in size from 250 to 400 nm, whose proportion did not exceed 0.02. Thus, the silver particles prepared by deposition from an organic solvent exhibit high stability under the catalytic process conditions. The lack of large particles with sizes above 500 nm is consistent with the fact that the sites of deep oxidation of ethylene glycol to CO₂ can be formed with participation of large silver particles. It should also be noted that, for the Ag/Si₃N₄-III-OI sample, the XFS examination did not reveal any significant loss of the active component after the reaction mixture exposure. The content of the active component on the support remained unchanged.

medium is the most stable and active. Enhanced selectivity with respect to glyoxal can be associated with uniform size of the active component particles which are evenly distributed over the support surface. An important finding of our study is that we did not reveal any significant accumulations of carbon deposition products on the system surface. This fact suggests an essential role played by the nature and structural features of the support in carbon deposition adversely affecting the activity of the supported and bulk catalysts in partial oxidation of ethylene glycol.

General relationships in rormation of metal Particles. As known, chemical interaction between the support and the metal are essential in formation of active and stable nanoparticles [9, 11, 14, 22, 23]. Of special significance is the chemical affinity in the case of platinum catalysts supported both on the oxide surface [12–15, 23] and on silicon nitride. For example, the activity of silica-supported catalysts is lost via formation of PtO₂ and it subsequent sublimation in selective oxidation of methane. By contrast, alumina-supported Pt catalysts are fairly stable and active due to formation of a stable spinel structure ($PtAl_2O_4$), which stabilizes platinum on the support surface. The lack of chemical affinity of platinum for silicon nitride is responsible for a major (up to 70%) loss under the preparation conditions. It was shown that the performance characteristics of the silicon nitride-supported platinum systems strongly depend on the degree of dispersion of the active component. Weak chemical affinity of platinum to silicon nitride leads to weak interaction with the support and favors agglomeration and subsequent deactivation of the materials.

We showed that the properties of the palladium catalysts are determined by the phase composition of silicon nitride and chemical affinity. For example, the Pd catalyst supported on silicon nitride with the α -phase dominating is the most active and stable. The palladium metal particles have an average size of 4 nm and are uniformly spread over the support surface (Table 3, Fig. 5a). The Si₃N₄-I-supported palladium particles are agglomeration-resistant, as validated by the TEM and XPS data. High activity and stability of the Pd catalyst can be associated with the chemical interaction between Pd and the silicon nitride support. According to the XPS data, the $Pd3d_{5/2}$ binding energy for freshly prepared Pd/Si₃N₄-I catalyst exceeds that for neat Pd (335.9 against 335.2 eV). However, the shapes of the $Pd3d_{5/2}$ XPS peaks and the corresponding Auger spectrum are

Thus, the catalyst deposited from nonaqueous

comparable with those of metallic palladium rather than of oxidized Pd²⁺ state. After the catalytic reaction the Pd3 $d_{5/2}$ binding energy (337.3 eV) corresponds to the partially oxidized state of Pd^{2+} (PdO). The $Pd3d_{5/2}$ binding energy of 336.1 eV instead of 335.3-335.4 eV for Pd metal was also revealed for $(0.75 \text{ wt}\% \text{ Pd})/\alpha$ -Si₃N₄ catalyst [23], which value exceeds that for SiO_2 - and Al₂O₃-supported Pd. It should be noted that the binding energy for Pd/α -Al₂O₃ corresponds to that for neat Pd metal (335.2 eV). This is presumably associated with modification of the electronic and structural properties of Pd metal particles due to specific interaction of palladium with the α -phase of silicon nitride. A change in the electron density of the metal particles affects the adsorption of the reactants and the surface reaction mechanism. An increase in the electron density on the metal particles favors oxygen adsorption as species active in deep oxidation of methane. High activity of the palladium catalyst can also be due to a high rate of the redox (Pd \leftrightarrows PdO) reactions proceeding during catalysis.

The specific interaction between palladium and α -Si₃N₄, yielding active particles, can be associated with the elemental composition of silicon nitride surface. Analysis of the Si2p signal in the XPS spectra of α -Si₃N₄ showed that the chemical state of silicon in the SiO_r oxide contributes with 13% to the peak. It was calculated that the [N1s]: [Si2p] ratio of 1.36 does not correspond to the stoichiometry of neat Si₃N₄ ([N1s]:[Si2p] = 1.33). The surface oxygen enters in the composition of either surface nonstoichiometric silicon oxide or silicon nitride. The available structural data on α -Si₃N₄ suggest that this is, in fact, silicon oxynitride in which some nitrogen atoms are replaced by oxygen and there exist nitrogen of silicon vacancies [24]. A number of studies also showed that the α -Si₃N₄ structure could be stabilized by the appearance of Si³⁺ in the valencecompensated system with oxygen atoms [25]. This may be specifically responsible for a higher stability of the α -Si₃N₄ phase at high partial oxygen pressures and low temperatures [26, 27]. The presence of oxygen in the α -Si₃N₄ structure leads to strong chemical interaction between palladium and the support.

A common feature of the palladium and silver catalysts consists in that the minimal size of the metal particle, the uniformity of deposition onto silicon nitride, and the activity of the active component are dependent on the nature of the precursor solution. We found that the hydrophobic/hydrophilic balance in the precursor solutions can be of decisive importance in formation of active particles. The presence of water can affect the chemical/elemental composition of the surface. Formation of palladium and silver particles in an aqueous solution proceeds by a mechanism different from that operating in the case of organic solution. This is responsible for formation of nanoparticles with different redox, adsorption, and catalytic properties. The use of an organic medium as solvent in the stage of preparation of the catalytic systems allows formation of an active catalyst for partial oxidation of ethylene glycol into glyoxal and deep oxidation of methane.

CONCLUSIONS

(1) The presence of amorphous fraction and β -Si₃N₄ modification in the support leads to formation of palladium particles that exhibit low activity in deep oxidation of methane. The most active and stable in deep oxidation reaction are palladium catalysts supported on Si₃N₄ with the α -phase dominating.

(2) The redox, adsorption, and catalytic properties of silicon nitride-supported palladium and silver nanoparticles are strongly dependent on the nature of the precursor solution utilized.

(3) The Pd and Ag systems prepared from an organic medium are highly active and stable in deep oxidation of methane and partial oxidation of ethylene glycol into glyoxal and are promising for preparation of catalytic composition thereof.

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