

Size Effect in the Oxidation–Reduction Processes of Platinum Particles Supported onto Silicon Dioxide

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Abstract—The interaction of the Pt/SiO₂ model catalysts as thin films on the surface of tantalum supports with a mixture of NO + O₂ (1 : 1) was studied by X-ray photoelectron spectroscopy. The pressure of the reaction mixture was varied from 6 to 64 mbar, and the temperature was varied from room temperature to 500°C. Two types of the catalysts, in which the Pt/Si atomic ratios were ~0.1 and ~0.3 (0.1-Pt/SiO₂ and 0.3-Pt/SiO₂, respectively) according to the XPS data, were studied. In 0.1-Pt/SiO₂, the particles of platinum predominantly had a size from 1 to 2.5 nm; a wide Pt particle size distribution in a range from 1 to 15 nm with a maximum at ~4 nm was characteristic of 0.3-Pt/SiO₂. The interaction of all of the samples with NO + O₂ at room temperature led to the dissolution of oxygen atoms in the bulk of platinum metal particles. As the reaction temperature was increased, PtO_x platinum oxide particles were formed: from small Pt particles in 0.1-Pt/SiO₂ at 300°C and from larger particles in 0.3-Pt/SiO₂ at 400–500°C. It was established that the reactivity of platinum oxide particles toward hydrogen also depended on the particle size. The small particles of platinum oxide were converted into platinum metal under the action of hydrogen (16 mbar) at 300°C. The coarse particles of PtO_x in the samples of 0.3-Pt/SiO₂ were reduced much more easily starting with room temperature.

Keywords: supported model catalysts, NO + O₂, hydrogen, platinum oxides, X-ray photoelectron spectroscopy

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INTRODUCTION

The oxidation number of platinum is a factor responsible for the activity of supported platinum catalysts. It was established that, in the NO_x storage reduction (NSR) systems, which are used for the neutralization of nitrogen oxides in exhaust gases, the catalyst loses its activity in the course of a key stage of the process: the oxidation of NO into NO₂, when platinum particles, which are the constituents of the catalyst, are converted into an oxidized state under the action of a reaction atmosphere. The ease of the conversion of supported platinum into the particles of platinum oxides depends on the nature of the support, the temperature, the composition of a reaction atmosphere, and the dispersity of platinum.

Lee and Kung [1] considered an example of the effect exerted by the size of platinum particles on their oxidation in the composition of a Pt/γ-Al₂O₃ catalyst. In a comparison of catalysts with platinum dispersity of 4.4 and 82% in the reaction of NO oxidation, it was found that the specific activity of the less dispersed catalyst was higher by two orders of magnitude. The reason for this behavior is that coarser platinum particles are less inclined to oxidation; therefore, platinum remains in an active metallic state in the course of

reaction in the case of a coarsely dispersed catalyst. Olsson and Fridell [2] found that the rate of NO₂ dissociation gradually decreased in the course of the interaction of Pt/Al₂O₃ with NO₂ at 350°C. With the use of X-ray photoelectron spectroscopy (XPS), it was established that the rate decreased due to the formation of platinum oxides. Because of this, the rate of catalyst deactivation in a reaction atmosphere containing NO₂ increased with the dispersity of platinum because smaller platinum particles were more easily converted into oxides. Benard et al. [3] found an analogous manifestation of the size effect for the Pt/SiO₂ catalysts: activity in the reaction of NO oxidation increased with the particle size of supported platinum. Mulla et al. [4] noted a fourfold increase in the activity of Pt/Al₂O₃ in the oxidation of NO at 300°C in a reaction atmosphere containing 300 ppm of NO + 170 ppm of NO₂ + 10% O₂ (the balance N₂) once a freshly prepared sample was subjected to sintering. Villani et al. [5] found the influence of the particle size of platinum supported onto different oxide carriers in a more complex catalytic process, which occurs with the participation of NO: the oxidation of carbon in an atmosphere containing NO, oxygen, and water vapor. They demonstrated that there is an optimum particle size of platinum for this process, 20–40 nm (at 3–4%

dispersity), which corresponds to an optimum particle size in the reaction of NO conversion into NO₂ in this reaction atmosphere.

Kalinkin et al. [6] used XPS and scanning tunnel microscopy (STM) for studying the interaction of NO₂ with the particles of platinum evaporated onto the surface of highly oriented pyrolytic graphite at room temperature and a pressure of 3×10^{-6} mbar. It was found that, under these conditions, only small platinum particles of size ~ 2.5 nm underwent oxidation with the formation of PtO and PtO₂ particles, whereas larger particles (~ 5.5 nm) remained in a metallic state.

Previously, the interaction of the Pt/Al₂O₃ and Pt/SiO₂ thin-film model catalysts with a reaction mixture of 10 mbar of NO + 10 mbar of O₂ was studied in [7]. The size of platinum particles in the test samples was 1–3 nm. The oxidation of nanosized platinum particles under the action of a reaction atmosphere occurred only at elevated temperatures ($\sim 300^\circ\text{C}$). Interaction at room temperature also led to a change in the state of platinum particles, which was supposedly caused by the dissolution of oxygen atoms in the bulk of particles with the retention of their metal properties. It was found that oxygen dissolved in the particles of platinum metal entered into reaction with hydrogen much more easily than the particles of platinum oxide. In this work, we carried out a comparative XPS study of two Pt/SiO₂ model systems with different platinum particle size distributions in a reaction with a mixture of NO and oxygen and the subsequent reduction of the oxidized samples in hydrogen in order to examine the effect of particle size on the oxidation–reduction processes with the participation of supported platinum particles.

EXPERIMENTAL

The preparation of model catalyst samples, their treatment in a reaction atmosphere, and the measurement of XPS spectra were carried out on a VG ESCA-3 instrument (Vacuum Generators, the United Kingdom) at a residual pressure of $< 5 \times 10^{-9}$ mbar in the analytical chamber of the instrument. The XPS spectra were recorded with the use of the $K\alpha_{1,2}$ X-ray line ($h\nu = 1253.6$ eV) of nonmonochromatic MgK α radiation at an X-ray tube voltage of 8.5 kV and a current intensity of 20 mA. The pass energy of the analyzer corresponded to the parameter HV = 20 V. Before the experiments, the scale of binding energies of the spectrometer was calibrated based on the positions of the gold Au4f_{7/2} (84.0 eV) and copper Cu2p_{3/2} (932.6 eV) lines. The photoemission spectra were processed after Shirley background subtraction. In the determination of the exact values of the binding energies of photoemission lines, the Si2p line of silicon dioxide, whose binding energy was taken equal to 103.4 eV, was used as an internal standard. In this calibration procedure, the binding energy of the C1s line of amorphous carbon, which was accumulated on the sample surface in

the course of spectral measurements, varied within a range of 284.8–285.0 eV.

The samples of model catalysts were obtained in the preparation chamber of the spectrometer in accordance with a published procedure [8–10]. The thin films of SiO₂ were synthesized on the surface of tantalum foil by the vacuum evaporation of silicon followed by annealing in oxygen at a pressure of 10^{-5} mbar and a temperature of 300°C . The sample was heated by passing the current through the tantalum foil; the temperature was measured with the aid of a chromel–alumel thermocouple welded to the reverse side of the foil. The SiO₂ films formed ensured the almost complete screening of the photoemission lines of tantalum in the XPS spectra. This allowed us to conclude that the thickness of SiO₂ films was no smaller than 10 nm. Platinum was supported onto the surface of silicon dioxide by thermal evaporation in a vacuum. The platinum content of the samples was determined based on the intensity ratio of the photoelectron lines Pt4f and Si2p, from which the Pt/Si atomic ratio was calculated taking into account atomic sensitivity factors [11]. In the Pt4f spectra of the freshly prepared Pt/SiO₂ samples, the spin-orbital components Pt4f_{7/2} and Pt4f_{5/2} had an asymmetric shape with a tail elongated toward higher binding energies; this shape is characteristic of platinum metal. Along with the binding energy $E_b(\text{Pt } 4f_{7/2})$, the degree of line asymmetry, which is calculated in accordance with a published procedure [7], is important for evaluating the chemical state of platinum. In platinum oxides, the Pt4f_{7/2} and Pt4f_{5/2} lines are symmetrical.

We prepared and studied two series of samples with the relative platinum concentrations Pt/Si ≈ 0.1 (0.1-Pt/SiO₂ samples) and Pt/Si ≈ 0.3 (0.3-Pt/SiO₂ samples). The model catalyst samples were treated with a mixture of NO + O₂ (molar ratio, 1 : 1) in the preparation chamber at $30\text{--}500^\circ\text{C}$ and a pressure of 6–64 mbar. Then, the samples were transferred into the analytical chamber without contact with the atmosphere for the recording of XPS spectra. After treatment in the mixture of NO + O₂, the samples were reduced in hydrogen at $30\text{--}300^\circ\text{C}$ and a pressure of 16 mbar.

The particle size of platinum supported on SiO₂ was estimated by transmission electron microscopy (TEM) on a JEM-2010 instrument (JEOL, Japan) at an accelerating voltage of 200 kV and a lattice resolution of 0.14 nm.¹ For this purpose, the Pt/SiO₂ samples with the Pt/Si atomic ratios of ~ 0.1 and ~ 0.3 were prepared in accordance with the procedure described above by the sequential supporting of SiO₂ and Pt onto carbon films on copper gauzes, which are traditionally used as substrates in TEM.

¹ The TEM measurements and image processing were performed by V.I. Zaikovskii and E.Yu. Gerasimov, the staff members of the Borekov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences.

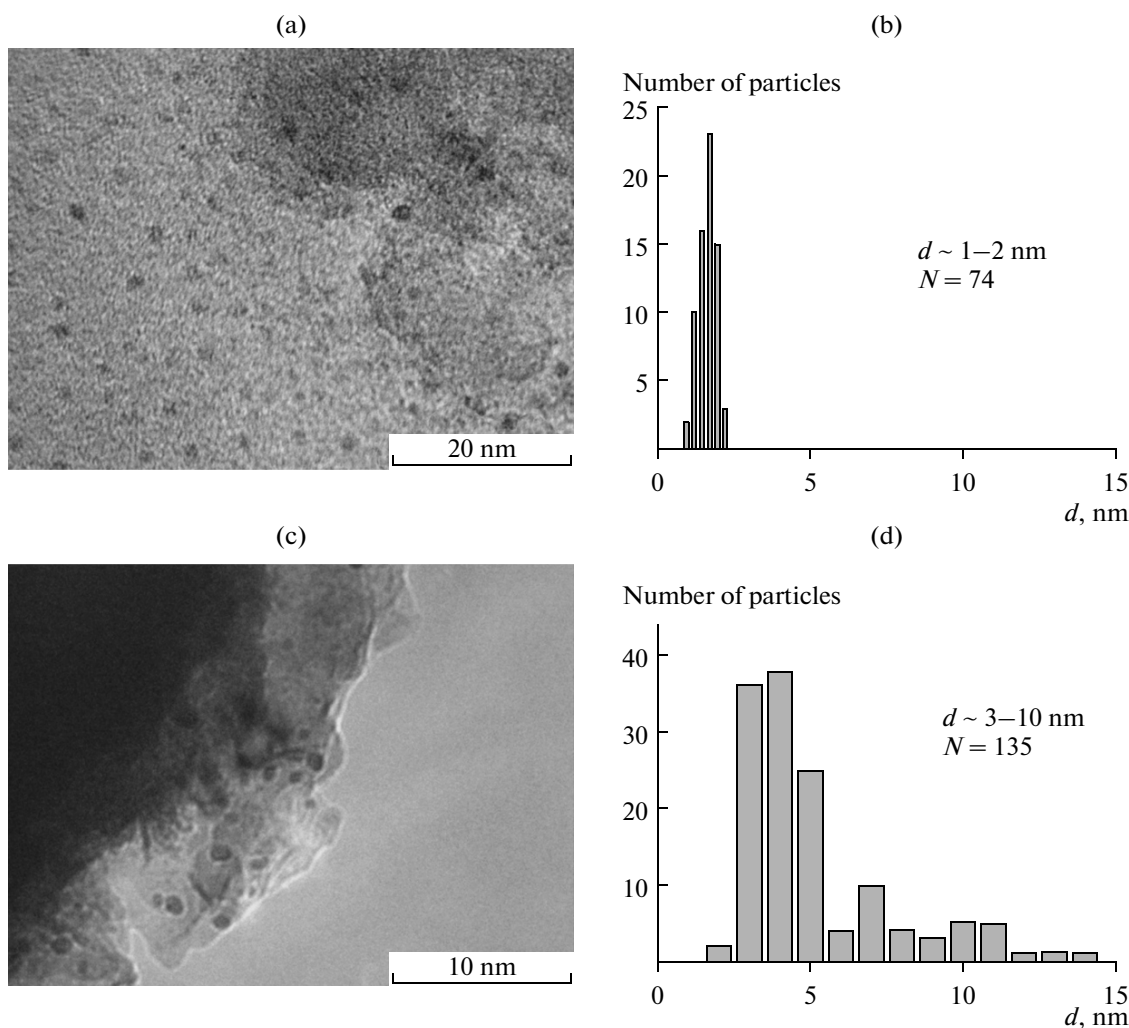


Fig. 1. TEM images of the thin-film (a) 0.1-Pt/SiO₂ and (c) 0.3-Pt/SiO₂ samples on carbon substrates and (b, d) the particle size distributions of platinum, respectively. N is the total number of particles taken into account in the plotting of the distributions.

RESULTS AND DISCUSSION

0.1-Pt/SiO₂ and 0.3-Pt/SiO₂ Samples in the Initial State

Figure 1 shows the TEM micrographs of the fragments of test model catalysts prepared on the substrates of a perforated carbon film. In the 0.1-Pt/SiO₂ sample with a relatively low platinum content (the Pt/Si atomic ratio ≈ 0.1) (Fig. 1a), the Pt particles have a narrow size distribution (Fig. 1b); in this case, the size of the majority of them falls in a range from 1 to 2.5 nm. In the 0.3-Pt/SiO₂ sample with a higher platinum content (the Pt/Si atomic ratio ≈ 0.3) (Fig. 1c), the evaporated metal particles have a wide size distribution (Fig. 1d). The distribution curve exhibits an asymmetrical peak with a maximum at ~ 4 nm and a strongly elongated tail toward greater particle sizes. A considerable portion of particles falls in a range from

3 to 5 nm, but particles whose size reaches 15 nm are also observed.

According to the XPS data, the binding energies $E_b(\text{Pt}4f_{7/2})$ in the 0.1-Pt/SiO₂ and 0.3-Pt/SiO₂ samples are 72.2 and 71.6 eV, respectively. The values obtained are noticeably different from the binding energy of bulk platinum metal, which is 71.2 eV. Nevertheless, based on the sample preparation method and taking into account the asymmetric line shape characteristic of bulk platinum in the Pt4f spectrum, we assume that platinum occurs in a metallic state. The shift of the Pt4f_{7/2} binding energy relative to a tabular value for platinum metal observed in the samples is explained by the final state effect related to photoemission from supported small metal particles. It is believed that the shift is caused by the fact that a positive hole at the 4f level, which results from photoemission, in the particles is screened less effectively than in the bulk metal; in this case, the smaller the particle size, the greater

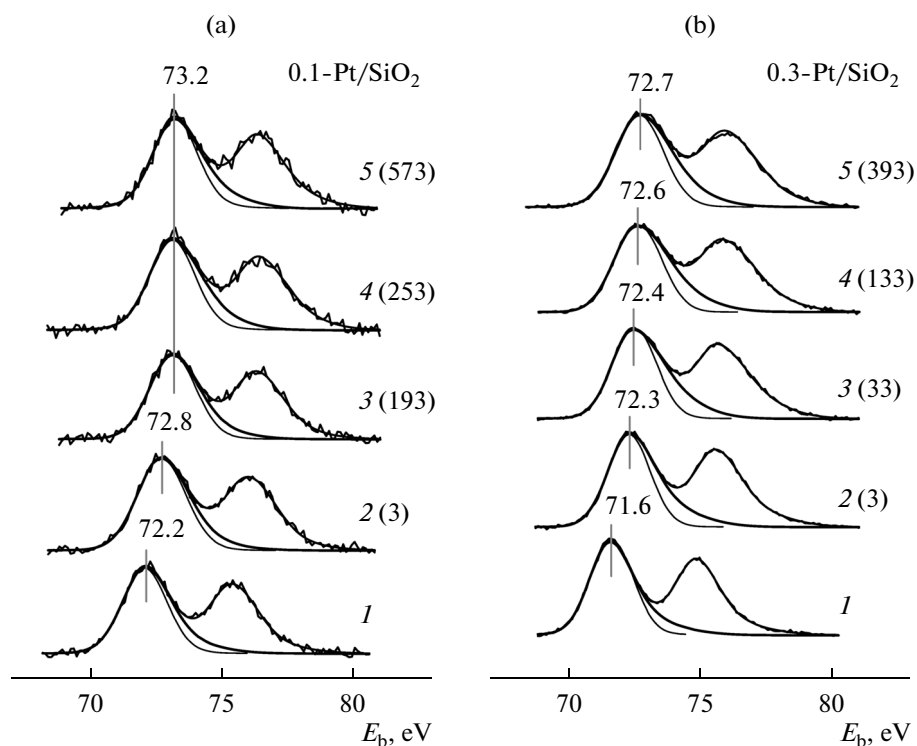


Fig. 2. Pt4f XPS spectra of the (a) 0.1-Pt/SiO₂ and (b) 0.3-Pt/SiO₂ samples (1) before and after interaction with a mixture of NO + O₂ at room temperature and exposures (mbar min) indicated in parentheses.

the shift [12]. In addition to the lines of platinum, the lines of silicon (Si2p, 103.4 eV and Si2s, 154.2 eV), silicon dioxide oxygen (O1s, 532.5 eV), and carbon from the substrate (C1s, 284.9 eV) can also be seen in the spectra. Analogous Pt4f, Si2p, Si2s, and O1s spectra were obtained for the samples prepared on the tantalum substrates.

Interaction of Platinum Particles with NO + O₂ at Room Temperature

The samples prepared on the tantalum substrates were used in the study of the interaction of the Pt/SiO₂ model systems with the reaction mixture (NO + O₂). The treatment of the samples in the reaction mixture did not lead to the appearance of lines in the N1s region and to changes in the O1s region. The most significant changes observed in the spectra are related to a change in the state of platinum. Figure 2 shows the Pt4f spectra measured after the contact of the 0.1-Pt/SiO₂ (Fig. 2a) and 0.3-Pt/SiO₂ samples (Fig. 2b) with the reaction mixture at room temperature. In each of the above spectra, a heavy line shows the asymmetrically shaped Pt4f_{7/2} component having a tail elongated toward greater binding energies. This asymmetric shape is characteristic of the photoemission lines in the spectra of platinum group metals; it is caused by the high density of *d* electrons at the Fermi level in them [13, 15]. To more clearly visualize the

asymmetry, a corresponding symmetrical line was drawn for each of the spectra in Fig. 2 by reflecting the left-hand half of an experimental component with respect to a vertical line that passes through a maximum.

Table 1 and Fig. 2a show changes in the parameters of the Pt4f line in the course of reaction of the 0.1-Pt/SiO₂ sample with NO + O₂ at room temperature. The total exposures given in the third column are the sums of the products of reaction mixture pressures (column 1) and contact times (column 2). Initially, $E_b(\text{Pt}4f_{7/2})$ rapidly increased with exposure, and it increased by ~1.0 eV at an exposure of 193 mbar min. The value of $E_b(\text{Pt}4f_{7/2})$ remained unchanged as the exposure was further increased. The line width and the Pt/Si atomic ratio did not change in the course of interaction, and the line shape remained asymmetric. Previously, a similar behavior of the XPS spectra of platinum in the model samples was interpreted as the dissolution of oxygen atoms formed upon the dissociation of NO (NO₂) in the bulk of supported metal particles [7, 8]. It is assumed that, in this case, platinum retained its metallic state, and an increase in the value of $E_b(\text{Pt}4f_{7/2})$ was caused by electron transfer from platinum atoms to dissolved oxygen atoms. Because the Pt/Si atomic ratio remained almost unchanged under the given conditions, it is believed that the dissolution of oxygen does not lead to the agglomeration

Table 1. Changes in Pt $4f_{7/2}$ line parameters and Pt/Si atomic ratios upon the contact of the Pt/SiO₂ samples with a mixture of NO + O₂ at room temperature

Pressure, mbar	Contact time, min	Total exposure, mbar min	E_b , eV	FWHM*, eV	Pt/Si	Asymmetry
0.1-Pt/SiO ₂						
0	0	0	72.2	2.2	0.10	1.34
6	0.5	3	72.8	2.3	0.11	1.23
6	5	33	73.1	2.2	0.10	1.27
12	5	93	73.1	2.3	0.11	1.24
20	5	193	73.2	2.2	0.10	1.24
20	3	253	73.2	2.3	0.11	1.35
64	5	573	73.2	2.2	0.11	1.31
0.3-Pt/SiO ₂						
0	0	0	71.6	2.0	0.34	1.26
6	0.5	3	72.3	2.2	0.34	1.53
6	5	33	72.4	2.4	0.36	1.50
20	5	133	72.6	2.5	0.35	1.47
20	5	233	72.6	2.5	0.37	1.48
32	5	393	72.7	2.5	0.37	1.45

* FWHM is the full width at half maximum.

of particles and does not have a noticeable effect on their size.

The interaction of 0.3-Pt/SiO₂ with NO + O₂ at room temperature was also accompanied by a monotonic increase in E_b (Pt $4f_{7/2}$) as the exposure was increased (Table 1, Fig. 2b). This sample is characterized by a wide platinum particle size distribution (Fig. 1d). It is obvious that, in this case, small particles (~1–2 nm) behave just as in 0.1-Pt/SiO₂; however, it is likely that the contribution of these particles to the integral Pt $4f$ peak is small. Thus, it is possible to state that, in this case, the basic contribution to the displacement of the Pt $4f$ line is ensured by relatively large particles (~3–15 nm), and the dissolution of oxygen in these particles also occurs effectively. Note that, in contrast to the 0.1-Pt/SiO₂ sample, upon the contact of 0.3-Pt/SiO₂ with the reaction mixture, the Pt $4f$ line was broadened and its maximum was simultaneously shifted (Table 1). In our opinion, this broadening is based on the structure peculiarities of the sample caused by the presence of platinum particles with different sizes on the support surface. It is believed that the saturation concentration of dissolved oxygen depends on particle size. For example, the smaller the particle, the more oxygen atoms per platinum atom can be dissolved. In this case, after the treatment of the 0.3-Pt/SiO₂ sample, the Pt $4f$ line in small particles will be more largely shifted than in large particles to cause the broadening of the integral line. As in the 0.1-Pt/SiO₂ sample, the absence of changes in the Pt/Si atomic ratio indicates that substantial changes in the particle size did not occur upon the interaction of the

0.3-Pt/SiO₂ sample with NO + O₂ at room temperature.

Oxidation of Platinum Particles on Interaction with NO + O₂ at Elevated Temperatures

Figure 3 shows the Pt $4f$ spectra of the 0.1-Pt/SiO₂ (Fig. 3a) and 0.3-Pt/SiO₂ samples (Fig. 3b) after contact with the mixture of NO and oxygen at elevated temperatures and a pressure of 64 mbar. The bottom spectra in Fig. 3 belong to the samples in the initial state, and they duplicate the bottom spectra in Fig. 2. The spectra arranged directly above them duplicate the top spectra in Fig. 2.

On the interaction of the 0.1-Pt/SiO₂ sample with a mixture of NO + O₂, an increase the temperature in a range from room temperature to 200°C did not change the position of the Pt $4f_{7/2}$ line (Fig. 3a); this fact indicates the absence of changes in the state of platinum particles. In this case, the line retained its asymmetric shape characteristic of the metallic state, although the degree of asymmetry decreased with temperature (Table 2). The line width also decreased in this case; this was likely due to the gradual leveling of dissolved oxygen concentration in different platinum particles before the stage of the formation of an oxide phase. As judged from small changes in the Pt/Si atomic ratio (Table 2), the particle size insignificantly changed in this case.

After treatment at 300°C, an additional shift of the Pt $4f_{7/2}$ line by ~0.4 eV toward greater E_b was observed (Table 2, Fig. 3a). The binding energy of 73.6 eV cor-

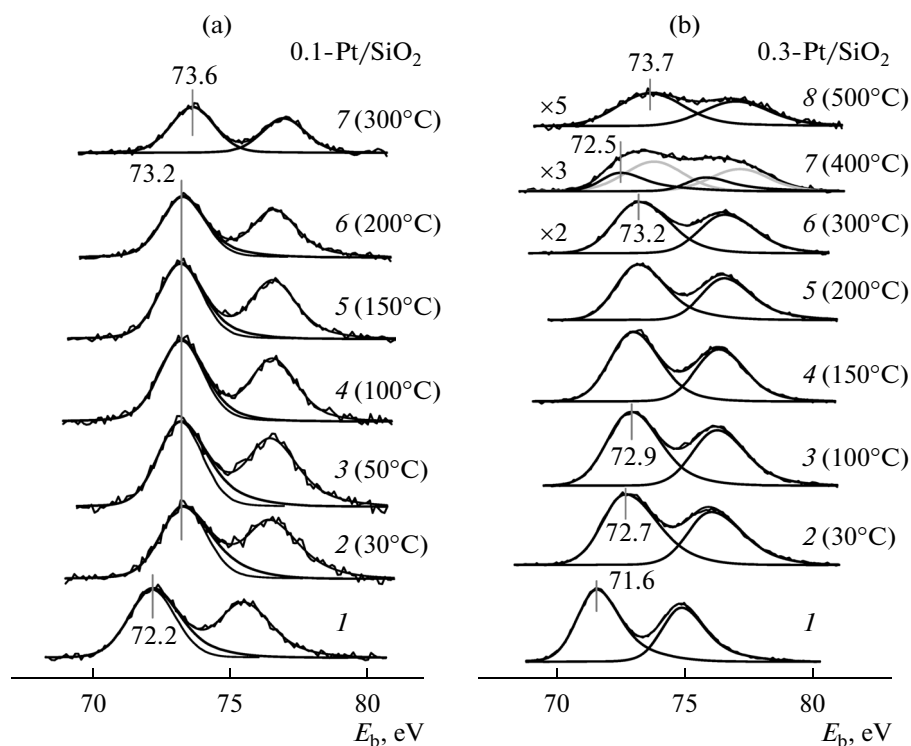


Fig. 3. Pt4f XPS spectra of the (a) 0.1-Pt/SiO₂ and (b) 0.3-Pt/SiO₂ samples (1) before and after interaction with a mixture of NO + O₂ at different temperatures.

responds to the oxidized state of platinum. It is difficult to accurately establish the nature of the oxide because a value of 73.6 eV occupies an intermediate position between the values characteristic of the bulk platinum oxides PtO and PtO₂ [15–18]. Subsequently, we designate this state as PtO_x. As expected, the Pt4f line became symmetrical upon the formation of platinum oxide particles (Table 2). The Pt/Si atomic ratio decreased by a factor of ~2, as compared with the value that characterized the sample in the initial state (Table 2). This can be due to a change in the size and shape of platinum particles upon their transfer into an oxidized state.

For the 0.3-Pt/SiO₂ sample in a temperature range from room temperature to 300°C, the Pt4f line gradually shifted to the region of high binding energies (Table 2, Fig. 3b). In a temperature range from room temperature to 200°C, a small narrowing of the Pt4f line with the retention of a significant degree of asymmetry occurred simultaneously with the shift. This behavior of the sample, which possesses a wide platinum particle size distribution, can be explained as follows: It is obvious that, as in the case of 0.1-Pt/SiO₂ with small platinum particles, an oxide phase was not formed in the 0.3-Pt/SiO₂ sample at a temperature lower than 200°C. It is believed that the concentration of dissolved oxygen in the larger particles of platinum increases with temperature. This leads to the leveling

of oxygen concentrations in the large and small particles and, as a result, to the narrowing of the Pt4f line.

Note that, after the reaction performed at 300°C, a large portion of platinum was not converted into oxide. After the reaction at 400°C, the shape of the spectrum considerably changed, and it could not be described by one doublet line. In Fig. 3b, a spectrum is decomposed into two doublet lines; the spin-orbital components of one of them are comparatively narrow and have an asymmetric shape (Table 2). The binding energy $E_b(\text{Pt}4f_{7/2})$ of this line is 72.5 eV. This value is close to $E_b(\text{Pt}4f_{7/2})$ after a contact of the sample with the reaction mixture at room temperature. The second line is relatively wide and symmetrical, and the binding energy $E_b(\text{Pt}4f_{7/2})$ corresponding to it is 73.7 eV, which is characteristic of the particles of platinum oxide (PtO_x) [7]. After an increase in the reaction temperature to 500°C, a spectrum that can be described by one doublet line with binding energy corresponding to oxide particles was obtained (Fig. 3b). The line is broad and almost symmetrical (Table 2). After the reaction at 500°C, the Pt/Si atomic ratio in the 0.3-Pt/SiO₂ sample decreased by almost an order of magnitude (Table 2); this fact suggests a considerable increase in the size of the particles as a result of their agglomeration.

Table 2. The temperature dependence of Pt $4f_{7/2}$ line parameters and Pt/Si atomic ratios on the contact of the Pt/SiO₂ samples with a mixture of NO + O₂*

T, °C	0.1-Pt/SiO ₂					0.3-Pt/SiO ₂				
	state of Pt	E _b , eV	FWHM**, eV	Pt/Si	asymmetry	state of Pt	E _b , eV	FWHM**, eV	Pt/Si	asymmetry
Initial Pt/SiO ₂	Pt ⁰	72.2	2.2	0.10	1.35	Pt ⁰	71.6	2.0	0.34	1.52
~30	Pt–O _{dis} ***	73.2	2.2	0.11	1.31	Pt–O _{dis}	72.7	2.5	0.37	1.45
50	Pt–O _{dis}	73.2	2.2	0.12	1.36	Pt–O _{dis}	72.7	2.5	0.34	1.39
100	Pt–O _{dis}	73.2	2.0	0.10	1.14	Pt–O _{dis}	72.9	2.4	0.35	1.22
150	Pt–O _{dis}	73.2	2.0	0.10	1.17	Pt–O _{dis}	73.0	2.3	0.30	1.24
200	Pt–O _{dis}	73.2	1.9	0.078	1.14	Pt–O _{dis}	73.2	2.3	0.23	1.23
300	PtO _x	73.6	1.9	0.049	1.00	Pt–O _{dis}	73.2	2.6	0.13	1.22
400	–	–	–	–	–	Pt–O _{dis}	72.5	2.1	0.076	1.76
						PtO _x	73.7	2.7		1.00
500	–	–	–	–	–	PtO _x	73.7	2.9	0.037	1.11

Dashes indicate that the 0.1-Pt/SiO₂ sample was not treated in the reaction mixture at temperatures of 400 and 500°C.

* The contact time of Pt/SiO₂ with a mixture of 32 mbar of NO + 32 mbar of O₂ was 5 min at all of the temperatures.

** FWHM is the full width at half maximum.

*** Pt–O_{dis} refers to the particles of platinum metal with oxygen dissolved in them.

Reduction of PtO_x Particles in Hydrogen

Figure 4 shows the Pt4f spectra of the 0.1-Pt/SiO₂ (Fig. 4a) and 0.3-Pt/SiO₂ samples (Fig. 4b) measured in the course of the reduction of platinum oxide particles, which were formed as a result of the preliminary oxidation of the supported particles of platinum metal in NO + O₂, in hydrogen. The bottom spectra characterize the samples in the initial state, and the spectra arranged above them were obtained after treatment in the reaction mixture at a temperature that leads to the formation of platinum oxide (PtO_x) particles.

It is evident that the treatment of the 0.1-Pt/SiO₂ sample in hydrogen in a temperature range from room temperature to 200°C did not have an effect on the spectral characteristics of the Pt4f line (Table 3, Fig. 4a). We can conclude that the particles of platinum oxide in the highly dispersed sample are not reduced by hydrogen under these conditions. As the reaction temperature was increased to 300°C, the position, shape, and intensity of the line changed. In this case, the spectrum was described by two doublet lines, the most intense of which belonged to the metallic state. In this doublet, the lines have a characteristic asymmetric shape (Table 3). The binding energy $E_b(\text{Pt}4f_{7/2})$ of 71.8 eV is lower than that in the sample in the initial state (72.2 eV). The weakening of the binding energy along with a decrease in the Pt/Si atomic ratio by a factor of ~2.5 unambiguously indicate that the particle size of platinum increased after oxidative and reductive treatments. The components of the second less intense doublet line have a symmet-

rical shape. The binding energy $E_b(\text{Pt}4f_{7/2}) = 73.5$ eV of this line is almost the same as that in the sample with oxidized platinum particles. Note that, in this case, we did not observe the state of dissolved oxygen. This result seems expected because the reactivity of oxygen dissolved in platinum is higher than that of oxygen in platinum oxide [7].

After treatment in NO + O₂ at 500°C, the 0.3-Pt/SiO₂ sample was characterized by the spectrum that consisted of one wide doublet line, which belongs to the oxide particles of PtO_x (Fig. 4b). Based on the fact that the 0.3-Pt/SiO₂ sample in the initial state had a wide platinum particle size distribution, we can hypothesize that the particles of PtO_x obtained as a result of interaction with NO + O₂ are also characterized by a wide size distribution. In contrast to the highly dispersed 0.1-Pt/SiO₂ sample, in this case, the reduction of oxide begins even at room temperature upon the addition of hydrogen. In this case, the initial spectrum is split into two doublet lines, one of which with a binding energy of 74.1 eV belongs to the oxide PtO_x, and it is likely that the other with an asymmetric shape of doublet components and $E_b(\text{Pt}4f_{7/2}) = 72.5$ eV belongs to metallic platinum, which contains dissolved oxygen (Table 3, Fig. 4b). As the reduction temperature was increased to 100°C, the qualitative composition of particles on the surface remained unchanged, but the fraction of platinum metal in the spectrum increased. Oxide was completely reduced to the metal after interaction with H₂ at 200°C. The binding energy $E_b(\text{Pt}4f_{7/2})$ after reduction was 71.6 eV,

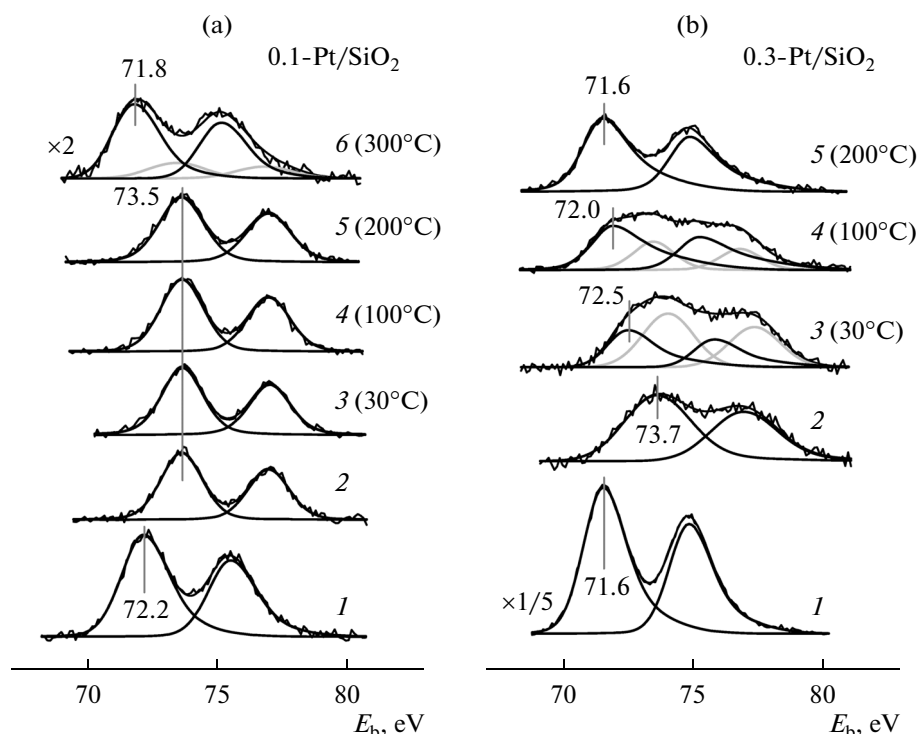


Fig. 4. Pt4f XPS spectra of the (a) 0.1-Pt/SiO₂ and (b) 0.3-Pt/SiO₂ samples (1) before and (2) after the oxidation of supported platinum particles in a mixture of NO + O₂ at (a) 300 and (b) 500°C and the subsequent reduction in hydrogen at different temperatures. Pressure of hydrogen, 16 mbar; interaction time, 2 min.

which coincides with the value determined for the initial sample. Note that the Pt/Si atomic ratio remained unchanged in the course of treatment in hydrogen. This fact allowed us to state that the particle size of supported platinum in the coarsely dispersed sample did not increase in the reduction process. It is interest-

ing that, in the finely dispersed sample, agglomeration was observed both at the stage of oxidation and as a result of the reduction of platinum nanoparticles; in the coarsely dispersed sample, the agglomeration of particles was noticeable only at the first stage of oxidation.

Table 3. The temperature dependence of Pt 4f_{7/2} line parameters and Pt/Si atomic ratios on the contact of the Pt/SiO₂ samples oxidized in a mixture of NO + O₂ with hydrogen

<i>T</i> , °C	0.1-Pt/SiO ₂					0.3-Pt/SiO ₂				
	state of Pt	<i>E</i> _b , eV	FWHM*, eV	Pt/Si	asymmetry	state of Pt	<i>E</i> _b , eV	FWHM*, eV	Pt/Si	asymmetry
PtO _x /SiO ₂	PtO _x	73.6	1.9	0.049	1.00	PtO _x	73.7	2.9	0.037	1.11
~30	PtO _x	73.6	1.9	0.052	1.00	PtO _x	74.1	2.3	0.039	1.00
						Pt–O _{dis} **	72.5	2.2		1.75
100	PtO _x	73.6	1.9	0.054	1.00	PtO _x	73.5	2.4	0.036	1.00
						Pt–O _{dis}	72.0	2.3		2.00
200	PtO _x	73.6	2.0	0.052	1.00	Pt ⁰	71.6	2.2	0.040	1.69
300	PtO _x	73.5	2.4	0.041	1.00	–	–	–	–	–
	Pt ⁰	71.8	2.2		1.24					

Dashes indicate that the 0.3-Pt/SiO₂ sample was not treated in hydrogen at a temperature of 300°C.

*FWHM is the full width at half maximum.

**Pt–O_{dis} refers to the particles of platinum metal with oxygen dissolved in them.

Thus, in this work, we discovered that the interaction of the Pt/SiO₂ model supported catalysts with a mixture of NO + O₂ led to the dissolution of oxygen atoms in the bulk of platinum metal particles and to the formation of platinum oxide (PtO_x) particles. A comparative study of the samples of two types of catalysts, which differed in the amounts of supported platinum and particle size distributions, showed that the dissolution of oxygen in platinum readily occurred even at room temperature regardless of particle size. At the same time, the conversion of platinum metal particles into oxide particles is an activated process, and the oxidation temperature decreases with decreasing the particle size. The ease of the reduction of the oxidized platinum particles in hydrogen also depends on the particle size: the larger the oxide particles, the lower the temperature at which they can be returned to the metallic state.

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REFERENCES

1. Lee, J.-H. and Kung, H.H., *Catal. Lett.*, 1998, vol. 51, p. 1.
2. Olsson, L. and Fridell, E., *J. Catal.*, 2002, vol. 210, p. 340.
3. Benard, S., Retailleau, L., Gaillard, F., Vernoux, P., and Giroir-Fendler, A., *Appl. Catal., B*, 2005, vol. 55, p. 11.
4. Mulla, S.S., Chena, N., Cumaranatunge, L., Blau, G.E., Zemlyanov, D.Y., Delgass, W.N., Epling, W.S., and Ribeiro, F.H., *J. Catal.*, 2006, vol. 241, p. 389.
5. Villani, K., Vermandel, W., Smets, K., Liang, D., van Tendeloo, G., and Martens, J.A., *Environ. Sci. Technol.*, 2006, vol. 40, p. 2727.
6. Kalinkin, A.V., Sorokin, A.M., Smirnov, M.Yu., and Bukhtiyarov, V.I., *Kinet. Catal.*, 2014, vol. 55, no. 3, p. 354.
7. Smirnov, M.Yu., Vovk, E.I., Kalinkin, A.V., Pashis, A.V., and Bukhtiyarov, V.I., *Kinet. Catal.*, 2012, vol. 53, no. 1, p. 117.
8. Smirnov, M.Yu., Kalinkin, A.V., and Bukhtiyarov, V.I., *J. Struct. Chem.*, 2007, vol. 48, no. 6, p. 1053.
9. Smirnov, M.Yu., Kalinkin, A.V., Pashis, A.V., Sorokin, A.M., Noskov, A.S., Bukhtiyarov, V.I., Kharas, K.S., and Rodkin, M.A., *Kinet. Catal.*, 2003, vol. 44, no. 4, p. 575.
10. Smirnov, M.Yu., Kalinkin, A.V., Pashis, A.V., Sorokin, A.M., Noskov, A.S., Kharas, K.C., and Bukhtiyarov, V.I., *J. Phys. Chem. B*, 2005, vol. 109, p. 11712.
11. Moulder, J.F., Stickle, W.F., Sobol, P.E., and Bomben, K.D., *Handbook of X-Ray Photoelectron Spectroscopy*, Eden Prairie, Minn.: PerkinElmer, 1992.
12. Mason, M.G., *Phys. Rev. B: Condens. Matter*, 1983, vol. 27, p. 748.
13. Hufner, S. and Wertheim, G.K., *Phys. Rev. B: Condens. Matter*, 1975, vol. 11, p. 678.
14. Stakheev, A.Yu., Shulga, Yu.M., Gaidai, N.A., Telegina, N.S., Tkachenko, O.P., Kustov, L.M., and Minachev, K.M., *Mendeleev Commun.*, 2001, vol. 5, p. 165.
15. Kaushik, V.K., *Z. Phys. Chem.*, 1991, vol. 173, p. 105.
16. Silvestre, A.J., Sepúlveda, E.A., Rodríguez, R.F., and Anderson, J.A., *J. Catal.*, 2004, vol. 223, p. 179.
17. Zafeiratos, S., Papakonstantinou, G., Jacksic, M.M., and Neophytides, S.G., *J. Catal.*, 2005, vol. 232, p. 127.
18. Huang, C.H., Wang, I.K., Lin, Y.M., Tseng, Y.H., and Lu, C.M., *J. Mol. Catal. A: Chem.*, 2010, vol. 316, p. 163.

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