

## **X-RAY PHOTOELECTRON SPECTROSCOPIC STUDY OF THE INTERACTION OF SUPPORTED METAL CATALYSTS WITH NO<sub>x</sub>**

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The reactions of the platinum and rhodium model catalysts applied to aluminum oxide with NO<sub>x</sub> (10 Torr NO + 10 Torr O<sub>2</sub>) were studied by X-ray photoelectron spectroscopy. The reaction conducted at room temperature formed on the surface of the oxide support the NO<sub>3,s</sub><sup>-</sup> nitrate ions characterized by the N1s line at 407.4 eV and O1s line at 533.1 eV and the NO<sub>2,s</sub><sup>-</sup> nitrite ions characterized by the N1s line with a binding energy of 404.7 eV. At the same time, the Pt4f and Rh3d lines of the supported platinum particles are shifted toward higher binding energies by 0.5-1.0 eV and 0.7-1.2 eV, respectively. It is assumed that the binding energies increase due to changes in the chemical state of the platinum metal in which oxygen is dissolved. The reaction of NO<sub>x</sub> with Pt/Al<sub>2</sub>O<sub>3</sub> at 200°C forms platinum oxide defined by the Pt4f<sub>7/2</sub> line with a binding energy of 72.3 eV.

**Keywords:** Pt/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> model catalysts, reaction with a mixture of NO and oxygen, surface nitrate ions, X-ray photoelectron spectroscopy.

### **INTRODUCTION**

Among substances emitted with exhaust gases of automobiles, carbon monoxide, hydrocarbons, and nitrogen oxides are most hazardous. Neutralization of the latter has become increasingly important in view of the new generation of gasoline motors, operating with a substantial excess of air in the working mixture [1, 2]. Therefore, it is important to create new catalytic systems specially designed for utilization of NO<sub>x</sub>; another challenge is investigation of the mechanism of interaction of NO and NO<sub>2</sub> with other components of the catalysts of exhaust gas detoxication.

The aim of the present work was an X-ray photoelectron spectroscopy (XPS) study of the nature of the products formed by the interaction of NO<sub>x</sub> with Pt/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> catalysts, which are the traditional components of the neutralizing mixtures of exhaust gases.

### **EXPERIMENTAL**

For experiments we used a VG ESCA-3 spectrometer (England) with a residual pressure of  $<5 \times 10^{-9}$  Torr in the analyzer chamber. X-ray photoelectron spectra were recorded using nonmonochromatic MgK<sub>α</sub> radiation ( $h\nu = 1253.6$  eV) obtained at a voltage of 8.5 kV and current 20 mA on the X-ray tube. The transmission potential of the energy analyzer

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corresponded to  $h\nu = 20$  V. Before the experiments, the binding energy scale of the spectrometer was calibrated against the metallic gold and copper lines,  $\text{Au}4f_{7/2}$  (84.0 eV) and  $\text{Cu}2p_{3/2}$  (932.6 eV). The photoemission spectra were processed after subtraction of the background approximated by the Shirley function. The binding energies (BEs) of the XPS lines were determined relative to the  $\text{BE}(\text{Al}2p)$  or  $\text{BE}(\text{Al}2s)$ , which were set at 74.5 eV and 119.3 eV, respectively, for aluminum oxide.

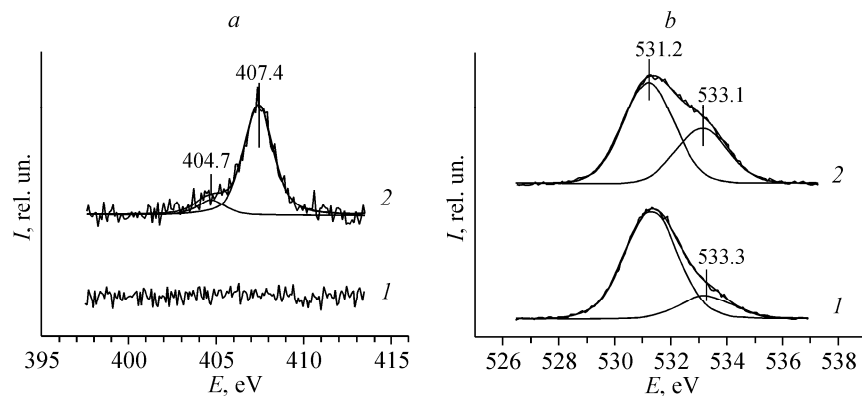
The model catalyst samples were obtained in the preparation chamber of the spectrometer using the procedure described in [3, 4]. The  $\text{Al}_2\text{O}_3$  samples were prepared as thin films by spraying metallic aluminum (in oxygen at a pressure of  $10^{-5}$  Torr) on a cleaned surface of tantalum foil. The film was additionally heated in oxygen and under vacuum at  $400^\circ\text{C}$ . The film was heated by passing alternate current through the tantalum foil; the temperature was measured with a chromel-alumel thermocouple sealed onto the foil. The  $\text{Al}_2\text{O}_3$  film thickness was  $\geq 100$  Å, as indicated by the nearly complete screening of the tantalum support lines. Platinum or rhodium was applied to the  $\text{Al}_2\text{O}_3$  surface by spraying the corresponding metal under vacuum. The Pt and Rh concentrations were determined from the Pt/Al and Rh/Al atomic ratios, which were calculated using the intensities of the Pt4f and Rh3d lines in the spectrum and taking into account the atomic sensitivity factor [5]. The model catalyst samples were processed in the preparation chamber in a mixture of  $\text{NO}_x$  (10 Torr  $\text{NO} + 10$  Torr  $\text{O}_2$ ) at a given temperature; thereafter they were removed (while kept out of contact with the atmosphere) to the analytical chamber for spectrum recording.

## RESULTS OF EXPERIMENTS

In the course of platinum spraying onto the thin film surface of alumina, a  $\text{Pt}4f_{7/2}$ – $\text{Pt}4f_{5/2}$  doublet appears and grows monotonically in the XP spectrum, overlapping the  $\text{Al}2p$  line. To evaluate the contribution of the  $\text{Al}2p$  line, we determined its parameters relative to the parameters of another characteristic line,  $\text{Al}2s$ , in the spectrum of  $\text{Al}_2\text{O}_3$ . Measurements on pure  $\text{Al}_2\text{O}_3$  films showed that the energy difference  $\Delta\text{BE} = \text{BE}(\text{Al}2s) - \text{BE}(\text{Al}2p)$  was  $44.8 \pm 0.05$  eV, and the intensity ratio between the  $\text{Al}2s$  and  $\text{Al}2p$  lines and their full width at half maximum (FWHM) was  $1.12 \pm 0.05$  and  $1.25 \pm 0.02$ , respectively. The binding energy and other parameters of the  $\text{Pt}4f_{7/2}$  line of the applied platinum particles were determined after subtracting the contribution of the  $\text{Al}2p$  line. As the platinum concentration on the alumina surface increases,  $\text{BE}(\text{Pt}4f_{7/2})$  decreases and the  $\text{Pt}4f$  line is narrowed. At a maximum platinum concentration, the binding energy of  $\text{Pt}4f_{7/2}$  becomes 71.1 eV, which is close to the value typical for metallic bulk platinum (71.2 eV) [5, 6]. For the minimum amount of applied platinum, when the Pt particle size is relatively small,  $\text{BE}(\text{Pt}4f_{7/2})$  is 72.4 eV. In previous studies, the binding energy of the  $\text{Pt}4f_{7/2}$  line also increased with the decreasing size of platinum particles when Pt was applied to other nonconducting oxide materials such as  $\text{TiO}_2$  [7, 8] and  $\text{SiO}_2$  [9]. For metal–nonconducting support systems, this is a common effect; it is generally associated with the final state effect that increases the binding energy of the core levels of the metal because of the less effective screening of the hole, arising from electron photoemission from these levels [10].

When Rh is sprayed onto the alumina surface, the spectrum acquires the  $\text{Rh}3d$  line; as the amount of applied rhodium increases, the binding energy of  $\text{Rh}3d_{5/2}$  changes from 308.2 eV to 307.4 eV. As in the case of Pt applied to  $\text{Al}_2\text{O}_3$ , the  $\text{BE}(\text{Rh}3d_{5/2})$  approaches the binding energy typical of the bulk metal (307.2 eV) at the maximum surface concentration of rhodium [5].

Before investigating the behavior of the model catalysts, we performed the reaction of  $\text{NO}_x$  with pure alumina. After the  $\text{Al}_2\text{O}_3$  film was treated in  $\text{NO}_x$  at room temperature, the XP spectrum acquired an intense  $\text{N}1s$  line with a binding energy of 407.4 eV, which belonged to the  $\text{NO}_3^-$  nitrate ions and a weak line with a binding energy of 404.7 eV attributed to the  $\text{NO}_2^-$  nitrite ions (Fig. 1a). In the region of  $\text{O}1s$ , the spectrum of the starting oxide contains two lines of which the stronger line has a binding energy of 531.2 eV characteristic of  $\text{Al}_2\text{O}_3$  and the weaker line with a binding energy of 533.3 eV can be assigned to the hydroxyl coating on the oxide surface ( $\text{OH}^-$ ,  $\text{H}_2\text{O}_s$ ) (Fig. 1b). After the reaction with  $\text{NO}_x$ , the second line increased considerably in intensity; this can also be explained by the formation of the nitrate and nitrite ions on the  $\text{Al}_2\text{O}_3$



**Fig. 1.** XPS spectra in the regions of (a) N1s and (b) O1s recorded (1) before and (2) after treatment with Al<sub>2</sub>O<sub>3</sub> in NO<sub>x</sub> (10 Torr NO + 10 Torr O<sub>2</sub>) at room temperature for 10 min.

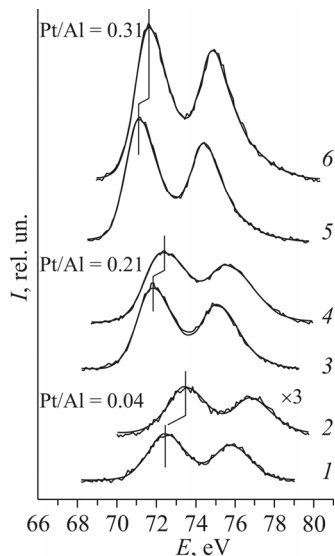
**TABLE 1.** N/Al and O/Al Atomic Ratios in the Nitrate Ions on the Surface of the Pt/Al<sub>2</sub>O<sub>3</sub> Samples with Different Concentrations of Applied Platinum after Their Treatment in NO<sub>x</sub> (10 Torr NO + 10 Torr O<sub>2</sub>) at Room Temperature for 10 min

Pt/Al atomic ratio	NO <sub>3,s</sub> <sup>-</sup> /Al atomic ratio	
	N/Al, ×3	O/Al
0	0.52	0.51
0.04	0.49	0.52
0.21	0.52	0.50
0.31	0.50	0.46

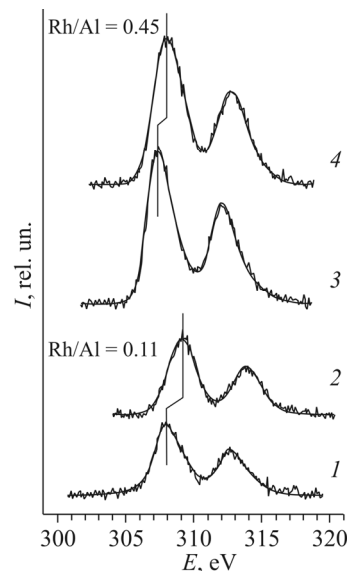
surface because the O1s line of these ions also appears in the given range of binding energies. Previously, it was reported (based on the vibrational spectroscopy data) that the interaction of Al<sub>2</sub>O<sub>3</sub> with a mixture of NO and oxygen under the conditions similar to those used in this work led to the formation of the nitrate and nitrite ions coordinated by the Al<sup>3+</sup> surface cations in different ways [11, 12].

When Pt/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> reacted with NO<sub>x</sub> at room temperature, the spectrum in the region of N1s acquired an intense line with a binding energy of 407.4 eV and a weak line with BE(N1s) = 404.7 eV; in the region of O1s, the line with BE = 533.1 eV became much stronger, which points to the formation of mainly the nitrate ions and a certain amount of the nitrite ions on the surface of Al<sub>2</sub>O<sub>3</sub>. The N/Al and O/Al atomic ratios, evaluated from the intensity data for the corresponding photoemission lines of the nitrate ions, showed that for the nitrates obtained both on pure alumina surface and on all catalyst samples with different amounts of platinum, the N/Al and O/Al ratios remained approximately constant (Table 1). Thus, the concentration of NO<sub>3,s</sub><sup>-</sup> achieved in the reaction with NO<sub>x</sub> was proportional to the fraction of the Al<sub>2</sub>O<sub>3</sub> surface that was free from the platinum particles.

Along with the formation of the nitrate and nitrite ions on the surface of the oxide support, the reactions of the model catalysts with NO<sub>x</sub> at room temperature led to changes in the binding energies of the Pt4f<sub>7/2</sub> and Rh3d<sub>5/2</sub> lines. Figure 2 shows the XPS spectra recorded in the region of Pt4f for Pt/Al<sub>2</sub>O<sub>3</sub> samples with different amounts of supported platinum before and after treatment in NO<sub>x</sub> at room temperature for 10 min. The binding energies and the FWHM of the Pt4f<sub>7/2</sub> line are listed in Table 2. In all cases shown in Fig. 2, the Pt4f line shifted by 0.5-1.0 eV toward higher binding energies after the reaction; the lower the platinum content in the sample, the larger the shift. The intensity and width of the Pt4f line remained almost unchanged during the interaction of Pt/Al<sub>2</sub>O<sub>3</sub> with NO<sub>x</sub> (Table 2). For very high contents of applied platinum (Pt/Al ~ 2), treatment in NO<sub>x</sub> did not lead to any significant changes in the Pt4f spectrum (Table 2).



**Fig. 2.** Pt4*f* XP spectra recorded for the Pt/Al<sub>2</sub>O<sub>3</sub> model catalysts with different surface Pt concentrations (1, 3, 5) before and (2, 4, 6) after treatment in NO<sub>x</sub> (10 Torr NO + 10 Torr O<sub>2</sub>) at room temperature for 10 min.



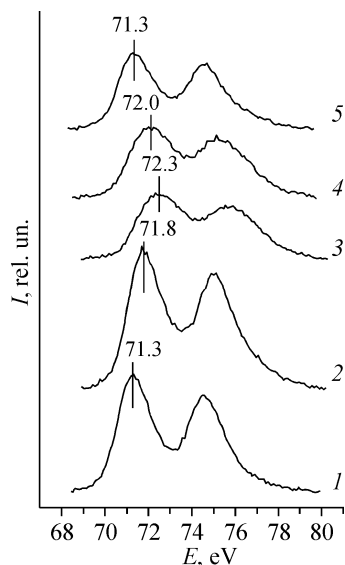
**Fig. 3.** Rh3*d* XP spectra recorded for the Rh/Al<sub>2</sub>O<sub>3</sub> model catalysts with different surface Rh concentrations (1, 3) before and (2, 4) after treatment in NO<sub>x</sub> (10 Torr NO + 10 Torr O<sub>2</sub>) at room temperature for 10 min.

**TABLE 2.** Changes in the Binding Energy and FWHM of the Pt4*f*<sub>7/2</sub> Line of the Pt/Al<sub>2</sub>O<sub>3</sub> Model Catalysts during Their Treatment in NO<sub>x</sub> (10 Torr NO + 10 Torr O<sub>2</sub>) at Room Temperature for 10 min

Pt/Al atomic ratio	Sample/treatment	Binding energy of Pt4 <i>f</i> <sub>7/2</sub> , eV	FWHM of Pt4 <i>f</i> <sub>7/2</sub> , eV	Pt/Al atomic ratio	Sample/treatment	Binding energy of Pt4 <i>f</i> <sub>7/2</sub> , eV	FWHM of Pt4 <i>f</i> <sub>7/2</sub> , eV
0.04	Pt/Al <sub>2</sub> O <sub>3</sub>	72.4	2.05	0.31	Pt/Al <sub>2</sub> O <sub>3</sub>	71.1	1.6
	+NO <sub>x</sub> , 30°C, 10 min	73.45	2.1		+NO <sub>x</sub> , 30°C, 10 min	71.6	1.6
0.21	Pt/Al <sub>2</sub> O <sub>3</sub>	71.8	1.9	~2	Pt/Al <sub>2</sub> O <sub>3</sub>	71.1	1.5
	+NO <sub>x</sub> , 30°C, 10 min	72.3	2.0		+NO <sub>x</sub> , 30°C, 15 h	71.2	1.5

The spectra in the region of Rh3*d* (Fig. 3) demonstrate changes during the reaction of NO<sub>x</sub> with Rh/Al<sub>2</sub>O<sub>3</sub> samples with different Rh/Al ratios. The numerical values of the binding energy and the FWHM of the Rh3*d*<sub>5/2</sub> line are listed in Table 3. The reaction of NO<sub>x</sub> with the samples whose Rh/Al ratio was 0.11 and 0.45 led to a shift of the Rh3*d* line by 1.2 eV and 0.7 eV toward higher binding energies; thus, the lower the rhodium content on the alumina surface, the larger the shift. At very high concentrations of applied rhodium (Rh/Al ~ 5.5), treatment in NO<sub>x</sub> did not cause any visible changes in the Rh3*d* spectrum.

Figure 4 demonstrates the temperature effect on the Pt4*f* spectrum of the applied platinum particles after treatment of the Pt/Al<sub>2</sub>O<sub>3</sub> model catalyst (Pt/Al = 0.30) in NO<sub>x</sub>. As in the case shown in Fig. 2, after the reaction of the catalyst with NO<sub>x</sub> at room temperature, the Pt4*f* line shifted by ~0.5 eV toward higher binding energies. It is important to note that higher reaction times did not cause any additional changes in the parameters of the Pt4*f* line (Table 4). Further reaction performed with the same composition of NO<sub>x</sub> at 200°C led to a shift of the line by another ~0.5 eV. At the same time, the line became considerably broadened (Table 4) and decreased by ~30% in intensity. According to the intensity of the N1*s* line after



**Fig. 4.** Pt4f XP spectra recorded for the Pt/Al<sub>2</sub>O<sub>3</sub> model catalyst with a Pt/Al ratio of 0.30 (1) in the initial state, (2) after the reaction with NO<sub>x</sub> (10 Torr NO + 10 Torr O<sub>2</sub>) at room temperature and (3) at 200°C, and (4) after further heating under vacuum at 100°C and (5) 200°C.

**TABLE 3.** Changes in the Binding Energy and FWHM of the Rh3d<sub>5/2</sub> Line of the Rh/Al<sub>2</sub>O<sub>3</sub> Model Catalysts during Their Treatment in NO<sub>x</sub> (10 Torr NO + 10 Torr O<sub>2</sub>) at Room Temperature for 10 min

Rh/Al atomic ratio	Sample/treatment	Binding energy of Rh3d <sub>5/2</sub> , eV	FWHM of Rh3d <sub>5/2</sub> , eV	Rh/Al atomic ratio	Sample/treatment	Binding energy of Rh3d <sub>5/2</sub> , eV	FWHM of Rh3d <sub>5/2</sub> , eV
0.11	Rh/Al <sub>2</sub> O <sub>3</sub>	307.9	2.0	~5.5	Rh/Al <sub>2</sub> O <sub>3</sub>	307.3	1.6
	+NO <sub>x</sub> , 30°C, 10 min	309.1	2.4		+NO <sub>x</sub> , 30°C, 15 h	307.3	1.6
0.45	Rh/Al <sub>2</sub> O <sub>3</sub>	307.3	1.8				
	+NO <sub>x</sub> , 30°C, 10 min	308.0	2.2				

**TABLE 4.** Changes in the Binding Energy and FWHM of the Pt4f<sub>7/2</sub> Line of the Pt/Al<sub>2</sub>O<sub>3</sub> (Pt/Al = 0.30) Model Catalyst during Treatment in NO<sub>x</sub> (10 Torr NO + 10 Torr O<sub>2</sub>) at Room Temperature and 200°C and during Further Treatment under Vacuum

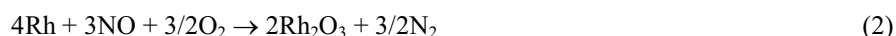
Treatment mode	Binding energy of Pt4f <sub>7/2</sub> , eV	FWHM of Pt4f <sub>7/2</sub> , eV	Treatment mode	Binding energy of Pt4f <sub>7/2</sub> , eV	FWHM of Pt4f <sub>7/2</sub> , eV
Starting Pt/Al <sub>2</sub> O <sub>3</sub>	71.3	1.6	NO <sub>x</sub> , 200°C, 60 min	72.3	2.2
NO <sub>x</sub> , 30°C, 10 min	71.8	1.7	Heating under vacuum, 100°C	72.0	2.1
NO <sub>x</sub> , 30°C, 40 min	71.8	1.7	Heating under vacuum, 200°C	71.3	1.7
NO <sub>x</sub> , 200°C, 10 min	72.1	2.1			

treatment of Pt/Al<sub>2</sub>O<sub>3</sub>, the nitrate ions formed in amounts several times smaller than in the reaction at room temperature. It is not excluded that the whole observed amount of the nitrate did not form during the reaction with NO<sub>x</sub> at a given temperature, but appeared during further cooling of the sample to room temperature in the reaction medium. Heating Pt/Al<sub>2</sub>O<sub>3</sub>, which was treated in NO<sub>x</sub> under vacuum at 100°C, led only to a slight (0.3 eV) shift of the Pt4*f* line to the region of smaller binding energies (Fig. 4, Table 4). The line shifted considerably as a result of heating under vacuum at 200°C, so that the binding energy reverted to its initial value, 71.3 eV. At the same time, it also narrowed to the initial value of FWHM (Table 4). The integrated intensity of the line did not change relative to the intensity of the catalyst treated in NO<sub>x</sub>.

## RESULTS AND DISCUSSION

As shown in the previous section, treatment of Pt/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> in NO<sub>x</sub> (10 Torr NO + 10 Torr O<sub>2</sub>) led to the formation of the nitrate and nitrite ions on the oxide support surface, on the one hand, and to considerably increased binding energies of the Pt and Rh core lines, on the other. The shift of the Pt4*f* and Rh3*d* lines by 1-1.5 eV is generally explained by the oxidation of the supported Pt and Rh particles [13]. In the bulk PtO and PtO<sub>2</sub>, the binding energy of Pt4*f*<sub>7/2</sub> was reported to be ~72.5 eV and ~74.5 eV, respectively [6, 13, 14]; in Rh<sub>2</sub>O<sub>3</sub>, the BE(Rh3*d*<sub>5/2</sub>) is ~308-309 eV [5, 15]. Thus, the shift of the Pt4*f* line to the BE(Pt4*f*<sub>7/2</sub>) = 72.3 eV and concurrent line broadening during the high-temperature treatment of the Pt/Al<sub>2</sub>O<sub>3</sub> model catalyst in NO<sub>x</sub> can be interpreted as resulting from the oxidation of the supported platinum particles to the state close to PtO (Fig. 4, Table 4). This conclusion is consistent with the results of [16], which reported the formation of a mixture of PtO and PtO<sub>2</sub> in the reaction of the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst with NO<sub>2</sub> at a pressure of 0.5 Torr and at 350°C according to XPS.

The oxidation of platinum metals with a mixture of NO and oxygen is a thermodynamically favorable process. Indeed, the changes in the standard thermodynamic potential  $\Delta G_{r,298}^0$  calculated from reference data for the reactions



are high negative values, -353.6 kJ/mol and -668.3 kJ/mol, respectively.

Nevertheless, despite the favorable thermodynamic characteristics of reactions (1) and (2), the formation of platinum metal oxides in the reactions of Pt/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> with NO<sub>x</sub> at room temperature is still open to discussion. The results presented in Figs. 2 and 3 and in Tables 2 and 3 show that the shift of the Pt4*f* and Rh3*d* lines in the reaction with NO<sub>x</sub> depends on the concentration of the supported metal on the oxide support surface. Because the average particle size increases with the surface metal concentration, it appears that the smaller the particles, the stronger the effect of treatment in NO<sub>x</sub>. At low concentrations of the metal on the Al<sub>2</sub>O<sub>3</sub> surface (Pt/Al = 0.04, Rh/Al = 0.11), the values of BE(Pt4*f*<sub>7/2</sub>) and BE(Rh3*d*<sub>5/2</sub>) obtained for the reactions of Pt/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> with NO<sub>x</sub> are within the ranges of the BEs typical for bulk platinum and rhodium oxides. At the maximum metal concentrations (Pt/Al ~ 2 and Rh/Al ~ 5.5), Pt4*f* and Rh3*d* lines do not shift in the reactions with NO<sub>x</sub> within the accuracy of the binding energy. For this case, the layer thickness *d<sub>i</sub>* of platinum and rhodium [17] was estimated at *d<sub>Pt</sub>* ≈ 10 Å and *d<sub>Rh</sub>* ≈ 22 Å; therefore, for these samples, the platinum metal is expected to form a continuous film similar to the bulk metal on the alumina surface. For the intermediate concentrations of applied Pt (Pt/Al = 0.21, 0.31) and Rh (Rh/Al = 0.45), the Pt4*f*<sub>7/2</sub> and Rh3*d*<sub>5/2</sub> lines are shifted, after the reaction with NO<sub>x</sub>, to the binding energies lying between the characteristic values of metals and oxides.

Based on the results obtained, we can assume that the oxidation of the applied particles of the platinum metal differs from the oxidation of the corresponding bulk metals. The oxidation of the bulk metal forms an oxide film on the metal surface, and the film thickness increases with the degree of oxidation, while the electronic properties of the metal under the oxide film do not change. The XP spectra then show two lines corresponding to the metal and oxide and shifted by ≥1-1.5 eV relative to each other on the energy scale. The case is different for the oxidation of small platinum metal particles under consideration. Treatment of the catalyst in NO<sub>x</sub> leads to a single state of platinum or rhodium, for which the BE(Pt4*f*<sub>7/2</sub>) or BE(Rh3*d*<sub>5/2</sub>) is intermediate between the corresponding values typical for the metal and oxide. One can assume that oxygen

dissolves in the platinum metal particles at the start of oxidation, and the solute oxygen atoms are distributed uniformly throughout the particle. In this case, the metal photoemission lines are expected to shift monotonically toward high binding energies at high solute oxygen concentrations, which is just observed in experiment. In the case of supported platinum, however, the Pt4*f* line width remained constant after the reaction (Table 2), which indicates that the platinum atoms remained in a single state in the catalyst.

According to the concept of oxygen solution in the supported platinum metal particles, the shift of the Pt4*f*<sub>7/2</sub> and Rh3*d*<sub>5/2</sub> photoemission lines must depend on the oxygen concentration in the metal particles achieved under the experimental conditions. The monotonous decrease in the shift of the Pt4*f*<sub>7/2</sub> and Rh3*d*<sub>5/2</sub> lines at higher metal concentrations observed in this work probably indicates that the ability of platinum and rhodium particles to dissolve oxygen decreases as the particle size increases. It is important that the NO<sub>x</sub> exposure times of more than 10 min at room temperature did not increase the Pt4*f*<sub>7/2</sub> binding energy further, as was the case with the Pt/Al<sub>2</sub>O<sub>3</sub> model catalyst (Table 4). The transition from the solution of oxygen atoms in the metal to the oxide phase is obviously activated because it demands a rearrangement of the crystal lattice and thus cannot be realized at room temperature.

To explain the observed behavior of the photoemission lines of platinum and rhodium, one can use another concept, which is based on changes in the catalyst surface potential as a result of its interaction with NO<sub>x</sub> at room temperature. The alumina surface initially contains a hydroxyl coating corresponding to the line with a binding energy of 533.1 eV in the O1*s* spectrum. The hydroxyl coating creates a certain potential on the initial oxide surface. The reaction with the mixture of NO and oxygen mainly forms the nitrate ions on the surface, due to which the Al<sub>2</sub>O<sub>3</sub> surface potential changes. If we assume that the surface potential becomes higher negative, this should decrease the measured binding energies of the lines of alumina, including the Al2*p*, Al2*s*, and O1*s* lines (oxide), and of the N1*s* and O1*s* lines of the nitrate ions (nitrate). The binding energies of the supported metal lines were determined from the relation for the BE(Al2*p*) of rhodium and from the relation for the BE(Al2*s*) of platinum. For example, the BE(Pt4*f*<sub>7/2</sub>) was determined from the formula

$$\text{BE}(\text{Pt}4f_{7/2}) = \text{BE}^*(\text{Pt}4f_{7/2}) - \text{BE}^*(\text{Al}2s) + 119.3 \text{ eV},$$

where BE\*(Pt4*f*<sub>7/2</sub>) and BE\*(Al2*s*) are the measured (apparent) binding energies of the corresponding lines. From the above formula it follows that a decrease in BE\*(Al2*s*) should lead to an increase in BE(Pt4*f*<sub>7/2</sub>) because of the decrease in the surface potential. Thus, because of the change in the Al<sub>2</sub>O<sub>3</sub> surface potential due to the formation of the nitrate ions on it, one would expect an apparent shift of the Pt4*f* and Rh3*d* lines toward high binding energies, which is not associated with changes in the chemical state of the supported platinum metals.

At higher concentrations of the applied metal, the fraction of the free surface of Al<sub>2</sub>O<sub>3</sub> decreases along with the concentration of the surface nitrate ions achieved in the reaction of the model catalyst with NO<sub>x</sub> at room temperature, which is consistent with the data of Table 1. The decrease in the NO<sub>3</sub><sup>-</sup> concentration, in turn, should lead to a decrease in the absolute value of the negative potential acquired by the surface. In this case, the higher the concentration of the surface nitrate ions and, accordingly, the lower the content of the applied platinum metal, the stronger the shift of the platinum and rhodium lines. This is consistent with the data obtained in this work (Figs. 2 and 3, Tables 2 and 3).

While the assumption about the effect of the potential acquired by the oxide (Al<sub>2</sub>O<sub>3</sub>) support surface on the binding energy of the Pt4*f*<sub>7/2</sub> and Rh3*d*<sub>5/2</sub> lines is quite reasonable, it still conflicts with the results obtained previously in our study of the reaction of the Pt/Al<sub>2</sub>O<sub>3</sub> model catalyst, obtained by a similar procedure, with a mixture of SO<sub>2</sub> (2 Torr) and oxygen (2 Torr) [3]. When the reaction was conducted at 300-400°C, the sulfate ions formed on the alumina surface; the SO<sub>4</sub><sup>2-</sup> concentrations achieved in [3] and the NO<sub>3</sub><sup>-</sup> content obtained in this work and defined by the S/Al and N/Al atomic ratios were close (0.1-0.15). By analogy with the nitration of the Al<sub>2</sub>O<sub>3</sub> surface sulfated in the reaction with an SO<sub>2</sub> + O<sub>2</sub> mixture, one would also expect the formation on the surface of a negative potential that could shift the Pt4*f* line toward high binding energies. However, the binding energy of Pt4*f*<sub>7/2</sub> determined relative to BE(Al2*s*) in the reaction of Pt/Al<sub>2</sub>O<sub>3</sub> with SO<sub>2</sub> + O<sub>2</sub> retained its constant value, 71.3-71.4 eV, typical of the supported platinum metallic particles. Evidently, the difference

between the two reaction media,  $\text{NO} + \text{O}_2$  and  $\text{SO}_2 + \text{O}_2$ , lies in the fact that the former has oxidating properties, while the latter has not. Thus, the hypothesis about changes in the chemical state of the platinum metal is preferable for explaining the behavior of the Pt4f and Rh3d lines in the reactions of the Pt/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> model catalysts with NO<sub>x</sub> at room temperature. The changes in the chemical state are currently attributed to the dissolution of the oxygen atoms in the supported platinum metal particles.

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