Genesis of the Active-Component Precursor in the Synthesis of Pt/Al$_2$O$_3$ Catalysts: III. Transformations of Adsorbed Platinum Complexes during Drying

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Abstract—The transformations of platinum(IV) complexes subsequent to their sorption on the support are considered. As the Pt(IV)/Al$_2$O$_3$ systems are dried at 25°C in daylight, their dehydration is accompanied by the replacement of inner sphere ligands of Pt(IV) by OH groups and the Coulombic bonding between the adsorbed metal complexes and the support turns into coordination bonding. Drying at a higher temperature of 120°C does not increase the extent of hydrolysis of the bound complexes in the predried samples. The observed increase in the proportion of unreadily reducible platinum species is likely due to the multisite adsorption of platinum complexes taking place.

An analysis of recent molecular-level studies of the transformations of precursors in the synthesis of adsorption-type catalysts, including the H$_2$[PtCl$_6$]–Al$_2$O$_3$ system, has revealed an interesting circumstance. In the study of the multistep synthesis of the catalysts, main attention has been focused on the initial stage (fixation of metal complexes on the support surface [1–7]) and on the final synthesis processes (calcination for converting the precursors in their oxide phase [8–12] and the reduction of the metal ions yielding a dispersed metal phase [13–17]). The drying of the catalysts, which is an indispensable step in catalyst preparation, has almost not been considered from the standpoint of chemistry. Thus, researchers have unintentionally ignored the possibility of controlling the molecular composition of the precursor at the drying stage and have disregarded the significance of the chemical composition and structure of metal complexes and the nature of their bonding with the support before the high-temperature heat treatment stage forming the properties of the finished catalyst.

Even in present-day publications, the drying of a material with a supported precursor compound in the temperature range from 25 to 200°C is often considered only as solvent removal from the pores of the support [18]. It is believed that the drying stage may play an important role only in the preparation of catalysts in which the precursor compound interacts weakly with the support. In this case, the removal of the solvent during drying causes transport of the compounds of the active metal to the evaporation surface, i.e., to pore mouths and to the outer surface of the granule. This may lead to the coarsening of the supported metal particles and to their nonuniform distribution in the granule bulk [16].

Only in a few studies was it demonstrated that the platinum complexes adsorbed on the oxide surface undergo further transformation at the drying stage. For example, using EXAFS and ^{195}Pt NMR spectroscopy, Shelimov et al. [1, 2, 19] established that, as model high-percentage [PtCl$_6$]$^{2-}$/Al$_2$O$_3$ samples are dried at 20°C, two chloro ligands of the chloroplatinate adsorbed on the alumina surface are replaced by two OH groups belonging to the support:

$$2Al-OH_2^{+\cdots}[PtCl_6]^{2-}$$
$$\leftrightarrow [(AlOH)_2PtCl_4]^0 + 2H_{ads}^+ + 2Cl_{ads}^-. \tag{I}$$
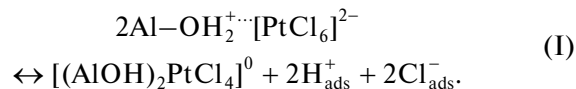
The formation of these inner-sphere complexes was indicated by the disappearance of the NMR signal as a consequence of the increase in chemical shift anisotropy caused by the heavy distortion of the octahedral symmetry of the environment of the central ion, Pt(IV). Raising the drying temperature to 90°C accelerates this process, which, according to Shelimov and his colleagues [1, 2, 19], is a thermally activated ligand substitution reaction. The results reported by these authors unambiguously indicate that the supported complexes undergo chemical conversions during drying. However, the processes occurring at this stage were described only at a qualitative level and particular chemical reactions were only postulated.

In our previous publications [20–23], we considered the transformations of platinum(IV) complexes in their interaction with the alumina surface at the impregnation stage. Here, we report quantitative data concerning the inner-sphere transformations of the

adsorbed platinum species and the mechanism of their binding at the catalyst drying stage and elucidate the role of chemical processes in the formation of the dispersed state of the supported metal.

EXPERIMENTAL

Sample Preparation

Samples containing 0.1–1.4 wt % metal were prepared by chemisorption of platinum(IV) complexes from an aqueous $H_2[PtCl_6]$ solution onto alumina. The solution-to-support volume ratio was 10. Chloroplatinic acid solutions (0.5×10^{-3}–10.0×10^{-3} mol/L) for deposition of the complex onto the support were prepared from the crystalline hydrate $H_2[PtCl_6] \cdot 6H_2O$ (AURAT Co., Soviet Specifications TU 6-09-2026-87).

The γ-Al_2O_3 used in the experiments, purchased from Condea, had a particle size of 0.1–0.2 mm, a specific surface area of $S_{BET} = 196$ m^2/g, an effective pore diameter of $D_{eff} = 11.1$ nm, and an adsorption pore volume of $V_{ads} = 0.51$ cm^3/g. The sodium and iron content was 0.003 and 0.021 wt %, respectively. The textural characteristics of the support were derived from nitrogen adsorption–desorption isotherms (77.4 K) recorded on an ASAP 2020 (Micromeritics) volumetric vacuum surface area and porosity analyzer. Differential pore size distribution curves were obtained by using the Barrett–Joyner–Halenda (BJH) method for the desorption branch. The unconnected cylindrical pores model was used in the calculations.

The platinum concentration in the solution before and after sorption was determined spectrophotometrically via a standard procedure [24]. Platinum was sorbed for 20 min. This time was sufficient for extracting the entire platinum from the solution. The dissolution of the surface layer of the support and the passage of Al^{3+} into the solution could be neglected owing to the very low rate of this process [25]. Next, the granules were thoroughly washed with water for removing non-chemisorbed components of the solution from the pore space of the support.

Water content data for samples dried for different times were obtained using a halogen moisture analyzer (Mettler Toledo). The sample weight for moisture determination was 1.0 g.

Sample Characterization Techniques

Gradient elution (GE). The GE method was used to quantitatively differentiate the surface complexes according to their chemical composition and the character of their interaction with the alumina surface. Two variants of this technique were used, which are detailed in our earlier publications [20–23]. In the first variant, the eluent consisted of acids differing in basicity and in strength of sorption on alumina (perchloric, oxalic, and citric acids). In the second variant, the bound anionic complexes of platinum were desorbed by varying the acidity of the support surface by treating the sample with an eluent with a progressively increasing pH value. This was done by gradually adding an alkaline agent (0.5 M sodium carbonate solution) to 0.2 M acetic acid. In the desorption experiments, we sampled the solution leaving the column to determine its platinum content. The platinum concentration data were used to plot desorption curves showing how platinum complexes are eliminated from the sample surface as the eluent passes through the column. After the desorption experiments, all samples were analyzed for residual, undesorbed platinum.

Diffuse reflectance electronic spectroscopy (DRES). The electronic spectra of powders were recorded on a UV-2501 PC spectrophotometer (Shimadzu) with an ISR-240A diffuse reflectance attachment. The spectra were measured against a $BaSO_4$ reflectance standard in the 11000–54000 cm^{-1} range with a resolution of 2 nm (500 cm^{-1}). Diffuse reflectance spectra were presented as the Kubelka–Munk function versus wavenumber.

[195]Pt magic angle spinning (MAS) NMR spectroscopy. The [195]Pt MAS NMR spectra of solid samples were recorded on an Avance-400 NMR spectrometer (Bruker) with an SB4 (MAS) multinuclear probe at a frequency of 86 MHz. The sample was placed in a zirconia rotor 4 mm in diameter and was spun at the magic angle (54°44') at a frequency of 10^4 Hz. The external standard was an aqueous 0.03 mol/L $H_2[PtCl_6]$ solution. The pulse duration was 13 μs; delay time before data digitization, 16 μs; pulse repetition interval, 0.7 s; sweep width, 70 kHz; number of data points per spectrum, 16000; total number of pulses, 4096.

Temperature-programmed reduction (TPR). H_2 and CO chemisorption technique. The hydrogen uptake and evolution processes were studied on an AutoChem II 2920 precision chemisorption analyzer with a thermal-conductivity detector. TPR experiments were carried out using a 10% H_2 + Ar mixture. The dispersion of supported platinum was determined using hydrogen or carbon monoxide as the probe molecule ($D(H_2)$ and $D(CO)$, respectively). The probe molecules were chemisorbed after TPR was complete and the catalyst was cooled to the preset temperature in a flowing inert gas. Pulses of a 10% H_2 + Ar or 9% CO + He mixture were introduced in the carrier gas (argon and helium, respectively) at regular time intervals. The mixtures were dosed at room temperature until the detector signal was constant. Calculating the dispersion of the metal, we accepted that the sorption stoichiometry is H : Me = 1 : 1 and CO : Me = 1 : 1 [26–28].

Testing the catalysts in low-temperature benzene hydrogenation. Benzene hydrogenation was carried out in a flow circulation reactor at an H_2: benzene molar ratio of 19 in the temperature range from 50 to 90°C at atmospheric pressure. Under these conditions, the only product of the reaction is cyclohexane and there is no noticeable coking of the catalyst sur-

Table 1. Sample designations and the results of the acid elution of the platinum complexes

Sample	Drying time in daylight, h	Desorbed Pt, wt %		Undesorbed Pt, wt %
		first peak	second peak	
1-00	0	74	15	11
2-01	1	50	22	28
3-24	24	31	27	42
4-48	48	23	24	53
5-72	72	17	23	60
6-96	96	18	23	59
7-140	140	22	22	56
8-240	240	15	19	66

Note: The supported platinum content is 0.3 wt %. The sample weight in the elution experiment is 4.0 g.

face. Before catalytic tests, the samples were heat-treated in an oxidative medium and in a reductive medium at 450°C. The results of these tests were presented as the dependence of the reaction rate on the partial pressure of benzene. From measurements taken at several temperatures, we estimated the activation energy of the reaction. The kinetic and adsorption data array enabled us to calculate the specific activity of the catalysts (turnover number, TON) as the number of benzene molecules converted on one surface atom of platinum per second. The number of surface platinum atoms was calculated from the percentage of the supported metal and its dispersion determined from CO or H_2 chemisorption data.

RESULTS AND DISCUSSION

Drying at 25°C (Aging)

Drying time effect on the chemical composition of adsorbed platinum complexes and on the strength of their interaction with the support. The objects of investigation were platinum(IV) complexes adsorbed on the γ-Al_2O_3 surface as a result of the interaction between alumina and an aqueous $H_2[PtCl_6]$ solution. The platinum content of the catalysts examined was 0.3 wt %, equal to that of the commercial platinum catalysts. The samples were dried at 25°C, and the drying time effect was studied. The sample numbers and the corresponding times of drying under daylight conditions are indicated in the sample designations (Table 1). The sample 1-00, which was dried until friable (for 2 h) at room temperature in the dark, was taken to be the reference sample. (It was demonstrated earlier that exposure of a chloroplatinate solution to daylight accelerates the hydrolysis of the complex [20].)

Under these drying conditions, the samples almost stopped losing their water in 5 h. For samples 1-00 and 2-01, the amount of water lost at temperatures up to 150°C (physically adsorbed water) was 27 and 20 wt %, respectively, and the water loss for the same samples predried for 5 h was 5 wt %. The water content of the

sample dried for 24 h (3-24) was 4 wt % and remained practically invariable as the drying time was further extended.

The effect of the drying time on the chemical composition of the metal complexes on the surface was studied by DRES. The diffuse reflectance spectra of the samples (Fig. 1a) indicate that the adsorbed chloroplatinate undergoes substantial transformations as the time of its contact with alumina is increased. The electronic spectrum of the reference sample 1-00 shows charge transfer bands characteristic of the $[PtCl_6]^{2-}$ [29, 30]. In the course of time, these bands shift to higher frequencies. The most pronounced changes in the spectrum take place in the first few hours, and almost no changes are observed after 50-h-long drying (Fig. 1b). This band shift is caused by the changes in the nature of the ligands in the coordination sphere of platinum, which lead to the formation of a mixture of metal complexes differing in the degree of substitution of Cl ligands by oxygen-containing ligands.
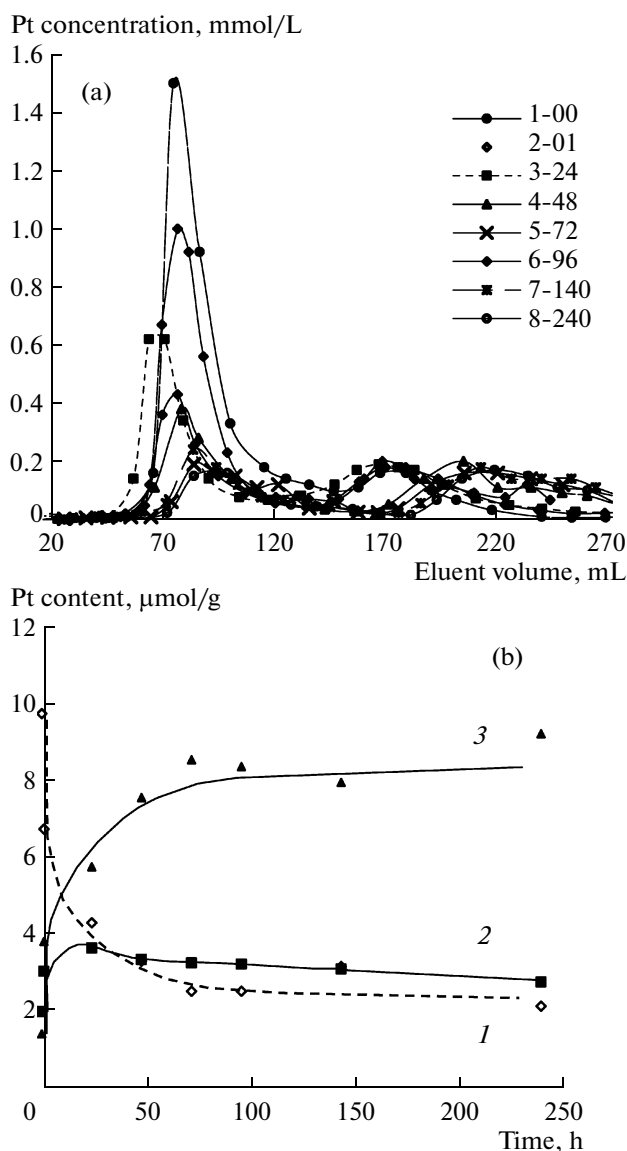
The changes in the chemical composition of the adsorbed platinum species are accompanied by a strengthening of the metal complex–support bonding, as is indicated by the gradient elution profiles for the adsorbed complexes under competing acid sorption conditions (Fig. 2a). According to these elution data, there are at least three platinum complex species adsorbed on the surface. Earlier, based on chemical analysis and spectroscopic data for the eluates and on DRES and EXAFS data for the adsorbed complexes, we determined the average chemical composition of each species and hypothesized that these species interact with the alumina surface in different ways [21].

It was established that, in the competing adsorption of anions [21], the most readily desorbable complexes are those which are close in composition to $[PtCl_6]^{2-}$ (first desorption peak). These ion-exchangeable species, which are likely held on the alumina surface by Coulomb forces, will be designated Pt_I. The second desorption peak is due to the removal of partially hydrolyzed complexes with the average compo-
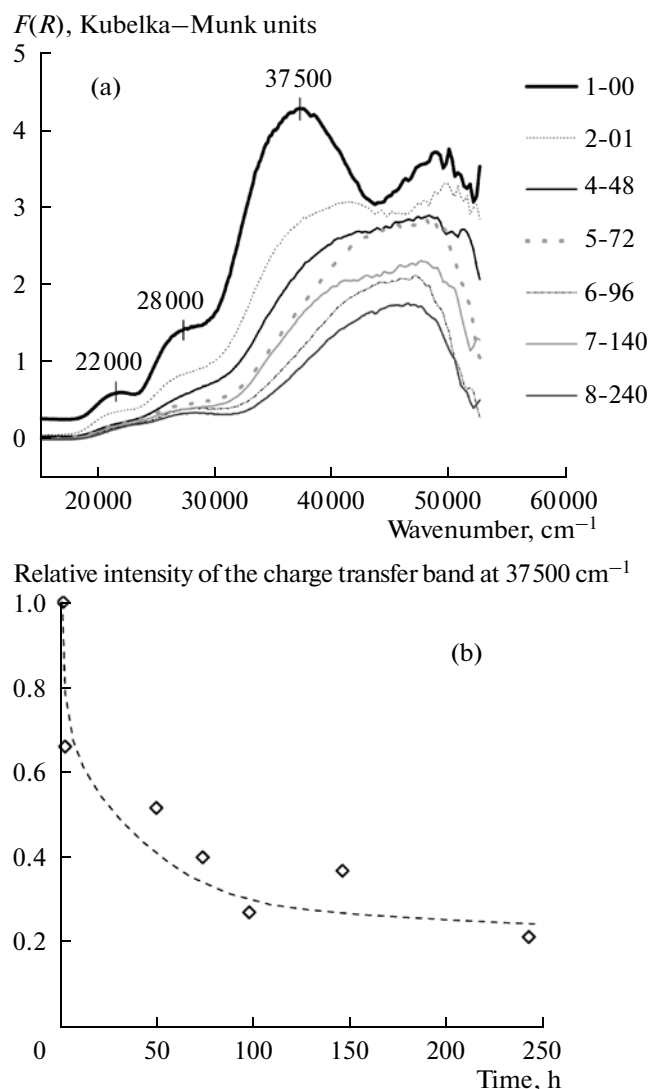
Fig. 1. (a) Diffuse reflectance spectra of the Pt(IV) chloro complexes adsorbed on γ-Al$_2$O$_3$ for the samples dried at 25°C for different times. (b) Time variation of the Cl $\rightarrow$ Pt charge transfer band at 37 500 cm^{-1}. The platinum content of the samples is 0.3 wt %.

**Fig. 2.** (a) Desorption (acid elution) profiles for H$_2$[PtCl$_6$]/Al$_2$O$_3$ dried for different times (drying temperature of 25°C, platinum content is 0.3 wt %). (b) Proportions of the desorbable and nondesorbable complexes as a function of the drying time: (*1*) first desorption peak, (*2*) second desorption peak, and (*3*) nondesorbable species.

sition PtCl$_4$O$_2$ [21]. Here, the eluent contains anions of oxalic (dibasic) and citric (tribasic) acids. Apparently, both electrostatic and coordination binding take place in the interaction of these platinum species (Pt$_{IC}$) with the support surface. The average composition of the nondesorbable species was determined to be PtCl$_2$O$_4$ [21]. The irreversibility of the sorption of the platinum complexes having more than two oxygen-containing ligands possibly indicates that the adsorbed chloroplatinate undergoes chemical transformation under the action of the surface hydroxo groups of the support. This transformation yields

coordinatively bound metal complexes (Pt$_C$) that are bonded to the support through bridging OH ligands.

The quantitative data of the desorption experiments (Table 1, Fig. 2b) demonstrate that the proportions of Pt$_I$, Pt$_{IC}$, and Pt$_C$ depend on the drying time and stop varying only after the sample is held for 50 h at room temperature. During drying, the proportion of the coordinatively bound chlorohydroxo complexes Pt$_C$ increases by a factor of about 5 to become 60%. The Pt$_{IC}$ complexes are likely intermediates in the reaction sequence

$$Pt_I \xrightarrow{k_1} Pt_{IC} \xrightarrow{k_2} Pt_C. \qquad (II)$$
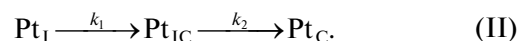
Provided that the amounts of all types of complexes are known (from gradient elution data) and their compositions are deduced (from EXAFS data [21]), it is possible to estimate how the average composition of the complexes changes with time. For example, it follows from the data presented in Table 1 that, immediately after platinum sorption, the average composition of the surface complexes is $PtCl_5O_1$ (74% $PtCl_6$ + 15% $PtCl_4O_2$ + 11% $PtCl_2O_4$). After 48-h-long drying, the average composition of the complexes is $PtCl_3O_3$ (20% $PtCl_6$ + 20% $PtCl_4O_2$ + 60% $PtCl_2O_4$). Note that the calculated average formula $PtCl_3O_3$ is confirmed by direct determination of the composition of the platinum complexes adsorbed on γ-Al_2O_3 by EXAFS spectroscopy [21, 22].

The buildup of nondesorbable platinum species in the course of drying was also indicated by desorption experiments at an increasing pH of the eluent for the samples with a higher platinum content of 1.4 wt % (Fig. 3, Table 2). As in the case of acid elution, the proportion of nondesorbable species in the elution experiments at an increasing pH grows to 50% as the drying time is extended (Table 2).

The finding that the outer-sphere complexes held by Coulomb forces turn into inner-sphere complexes coordinatively bound to the surface as water is removed from the material is confirmed by the ^{195}Pt MAS NMR data. This method does not allow samples with a low concentration of a supported precursor to be examined, so we prepared samples of chemisorbed platinum complexes with a Pt content of 4.5 wt %, which corresponds to the limiting sorption capacity of γ-Al_2O_3. The NMR data indicate that the binding of the platinum(IV) complexes to the support in the freshly dried sample (Fig. 4a) does not cause noticeable distortions in the geometry of the complexes and can be viewed as Coulomb interaction [31]. In this case, the adsorbed platinum species are the chloro complex $[PtCl_6]^{2-}$ (0 ppm) and the monosubstituted chlorohydroxo complex $[PtCl_5(OH)]^{2-}$ (640 ppm). Further drying of the sample in daylight (Fig. 4b) causes a marked decrease in the intensity of the second signal. This indicates a high reactivity of the hydrolyzed platinum species in subsequent transformations yielding strongly adsorbed species [22]. Prolonged drying is accompanied by extensive hydrolysis of the adsorbed chloro complexes, and this leads to an increase in the proportion of coordinatively bound complexes and, as a consequence, to the almost complete disappearance of the NMR signals (Fig. 4c).

Thus, the spectroscopic and desorption data provide further evidence that the conversion of the adsorbed platinum(IV) chloro complex during drying consists in an increase in the extent of its hydrolysis and in a change in the nature of the complex–support bonding.

Special-purpose measurements demonstrated that the amount of physically adsorbed water removable at $T < 150°C$ in the reference sample (1-00) is about
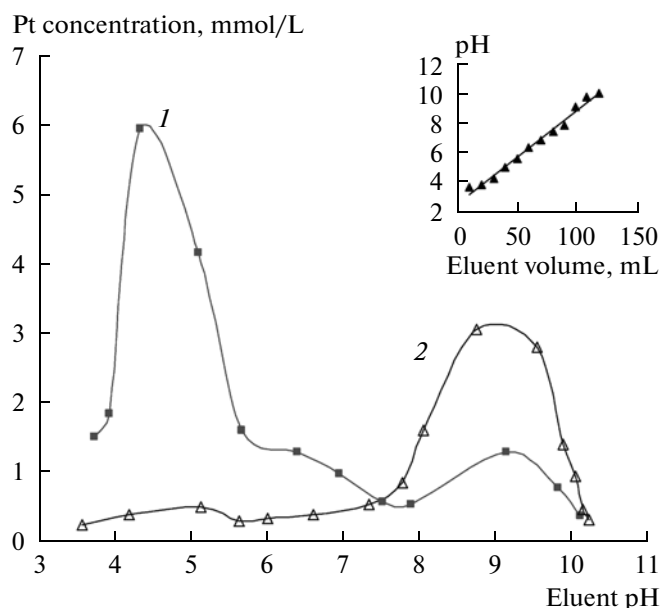
Fig. 3. Desorption profiles for $H_2[PtCl_6]/Al_2O_3$ at a varying pH of the eluent: (*1*) freshly dried sample and (*2*) sample dried at 25°C for 48 h. The platinum content of the sample is 1.4 wt %. Inset: variation of the eluent pH during desorption.

0.3 cm^3/g. This amount of water can fill up to 60% of the pore space of the support. The interaction of the platinum complexes with the surface under these conditions is likely Coulombic in nature, and the complexes adsorbed owing to this interaction may be in the same state as they are in solution [21]. These complexes are likely ion-exchangeable ones (Pt$_I$). They are hydrolyzed to a small extent, and their composition can be determined by ^{195}Pt MAS NMR spectroscopy.

The release of the greater part of physically adsorbed water as a result of 5-h-long drying at 25°C (with the water content of the sample decreasing from 30 to 5 wt %) causes the most significant changes in the interaction of the adsorbed complexes with the surface: the proportion of hydrolyzed, coordinatively bound complexes Pt$_C$ increases sharply (Fig. 2b). According to our pore size distribution data, only alumina pores smaller than 6 nm in diameter, which account for at most 10% of the total pore volume of the support, can be filled under these conditions. As

Table 2. Results of the elution of the platinum complexes at a varying pH of the eluent

Drying time in daylight, h	Desorbed Pt, wt %		Undesorbed Pt, wt %
	first peak	second peak	
1	63	10	27
48	11	42	47

Note: The supported platinum content is 1.4 wt %. The sample weight in the elution experiment is 4.0 g.
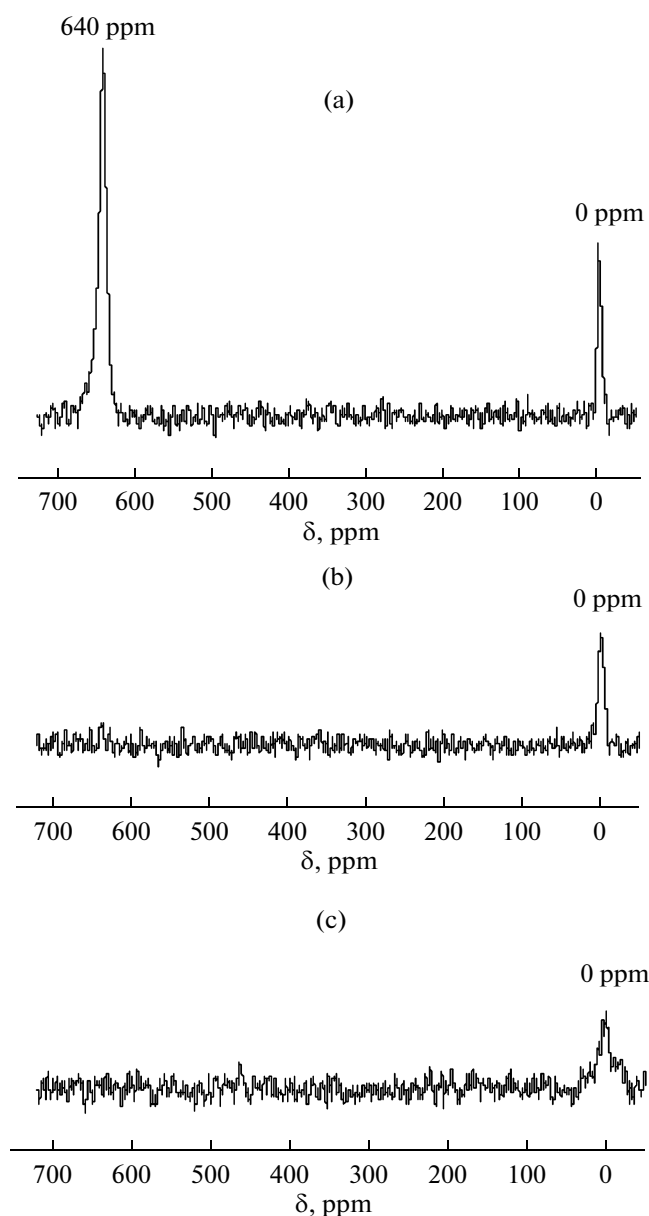
Fig. 4. ^{195}Pt MAS NMR spectra of platinum(IV) complexes in (a) the freshly dried sample (1-00), (b) the sample dried for 2 h in daylight, and (c) the sample dried for 6 h in daylight. The platinum content of the samples is 4.5 wt %.

the drying time is extended to 48 h, the release of physically adsorbed water slows down, the water content of the support remains at the 3−4% level, and the proportions of the different types of bound complexes

**Table 3.** Effective rate constants k_1 and k_2

Drying time, h	k_1, s^{-1}	$k_{2\,(mean)}$, s^{-1}
0−3	6.3×10^{-5}	3.3×10^{-4}
3−50	2.2×10^{-6}	8.6×10^{-6}
70−240	2.8×10^{-7}	1.4×10^{-6}

change to a lesser extent. Drying for a still longer time does not cause any noticeable changes in the water content, platinum desorption data, or spectral characteristics of the adsorbed complexes.

As the amount of physically adsorbed water decreases, hydrolysis takes place just in the near-surface layer, increasing the probability of the aquation of the adsorbed complexes. It is believed [32] that hydrolysis in the near-surface layer occurs more readily than hydrolysis in the solution bulk owing to the fact that the water molecules coordinated to the surface are more reactive as attacking ligands in the replacement of the acido ligand of the complex. It is the formation of these platinum aqua complexes that is considered to be the rate-determining step in the fixation of the complexes on the oxide surface [32]:

$$[PtCl_6]^{2-} + n\left(H_2O^{..}HO-Al\sim\right)$$
$$\leftrightarrow [PtCl_{6-n}(H_2O)_n]^{(2-n)-...}n(HO-Al\sim) + nCl^-. \quad (III)$$
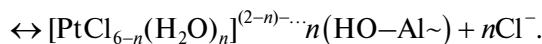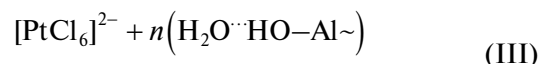
The final step of the fixation of the complexes is rapid ligand exchange between the adsorbed aquated complexes and OH groups of the Al$_2$O$_3$ surface, which yields platinum complexes coordinatively bound to the surface, Pt$_C$:

$$[PtCl_{6-n}(H_2O)_n]^{(2-n)-...}n(HO-Al\sim)$$
$$\leftrightarrow [PtCl_{6-n}(OH)_n-nAl\sim]^{(2-n)-} + nH_2O. \quad (IV)$$
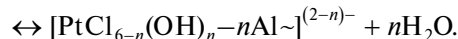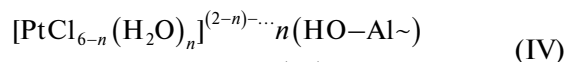
The consecutive reaction scheme (II) implies the following expressions for the disappearance of each particular type of complex [33]:

$$C(Pt_I) = C^0(Pt_I)e^{-k_1t}, \quad (1)$$

$$C(Pt_{IC}) = \frac{k_1}{k_2 - k_1}C^0(Pt_I)\left(e^{-k_1t} - e^{-k_2t}\right), \quad (2)$$

$$C(Pt_C) = C^0(Pt_I)\left[1 + \frac{k_1}{k_2 - k_1}e^{-k_2t} - \frac{k_2}{k_2 - k_1}e^{-k_1t}\right], \quad (3)$$

where $C(Pt_I)$, $C(Pt_{IC})$, and $C(Pt_C)$ are the concentrations of the ion-exchangeable, intermediate (aquated), and coordinatively bound platinum species, respectively, at the point in time t; $C^0(Pt_I)$, $C^0(Pt_{IC})$, and $C^0(Pt_C)$ are the initial concentrations of the ion-exchangeable, intermediate (aquated), and coordinatively bound platinum species, respectively; k_1 is the aquation rate constant; k_2 is the rate constant of the formation of coordinatively bound platinum species.

The rate constant of the first step of the conversion of the adsorbed complexes (aquation), k_1, can be determined from Eq. (1) under the assumption that the entire platinum is initially in the form of chlorine-rich platinum complexes, provided that the concentration of these complexes has been measured in the desorption experiment. Under the assumption that $k_1 < k_2$, which follows from the shape of curve *2* in Fig. 2b, it is possible to drop the term e^{-k_2t} in Eq. (2)

Table 4. Results of chemisorption measurements

| Sample	TPR data		$D(H_2)*$, %	$D(CO)*$, %
	hydrogen uptake, μmol/g	$\Sigma H_2/Pt$		
2-01	31.3	2.0	34	25
4-48	39.3	2.6	85	68
2-01 (dried at 120°C, 6 h)	50.5	2.8	86	56
2-01 (calcined at 400°C, 3 h)	28.2	1.6	85	63

Note: The supported platinum content is 0.3 wt %.

* $D(H_2)$ and $D(CO)$ are the dispersions of supported platinum determined using H_2 and CO chemisorption, respectively.

and to estimate the k_2 value. The calculated values of the rate constants are listed in Table 3.

It follows from the data presented in Table 3 that the transformations of the Pt(IV) chloro complexes adsorbed on the alumina surface are much faster than the transformations of the same complexes in a homogeneous medium. There are no quantitative kinetic data for $[PtCl_6]^{2-}$ hydrolysis in aqueous solution because of the very low rate of the process [30, 34]. Kinetic data available on the binding of platinum(IV) complexes to oxide surfaces are also scanty and are mostly qualitative [35]. However, the rate constant of $[PtCl_6]^{2-}$ hydrolysis on the yttrium oxyhydrate surface at 80°C is 8.85×10^{-5} s^{-1} [32] and is close to the values obtained by us for the $[PtCl_6]^{2-}-\gamma-Al_2O_3$ system.

In addition, it follows from the data presented in Table 3 that the effective rate constants of both steps decrease as the drying time is extended. This result can be explained both by the decrease in the amount of water coordinated to the surface (which is a reactant in the first step of the process—aquation of the adsorbed complexes) and in terms of the number and properties of accessible OH groups on the surface (which are involved in the second step—ligand exchange between the alumina surface and the aquated complexes).

Drying time effect on the reduction of platinum and its dispersion. The drying time effect showed itself in the TPR study of platinum reduction. For the freshly dried sample 2-01, which contained 50% Pt_I, 22% Pt_{IC}, and 28% Pt_C (Table 1), the TPR profile (Fig. 5a) showed three distinct reduction regions. A considerable part of hydrogen was taken up at low temperatures, with an uptake rate maximum occurring at 80°C. In addition, there were TPR peaks at 200°C and at higher temperatures (350°C). Thus, we observed the independent reduction of different platinum species, which is a fairly rare case. The reduction of part of the platinum began already during the formation of the baseline, so it was impossible to precisely determine the amount of hydrogen consumed in the reduction of the low-temperature species. Extending the drying
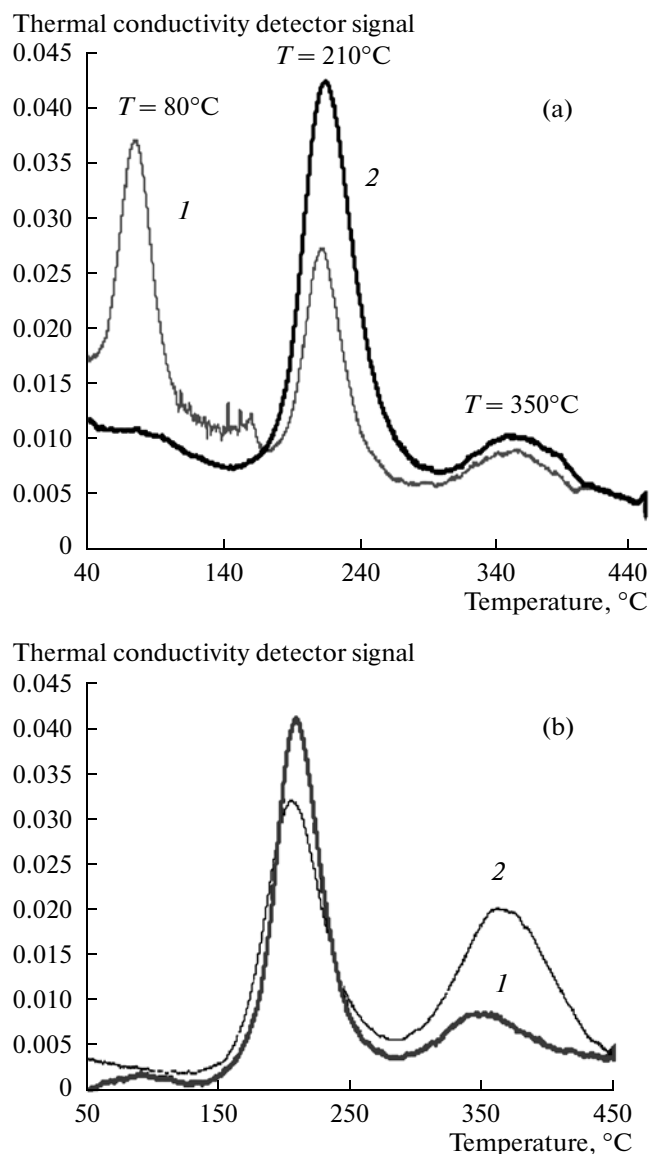
Fig. 5. (a) TPR profiles for the platinum(IV) complexes in samples differing in their drying time: (*1*) 2-01 and (*2*) 4-48. (b) The same for samples differing in their drying time and temperature: (*1*) 25°C, 48 h; (*2*) 120°C, 12 h. The platinum content of the samples is 0.3 wt %.

Table 5. Results of catalytic tests of the samples in low-temperature benzene (B) hydrogenation

Sample	k, s^{-1}			TON*, (molecule B) (atom Pt)$^{-1}$ s^{-1}			E_a, kcal/mol
	reaction temperature, °C			reaction temperature, °C			
	55	70	90	55	70	90	
1-00 (T_{H_2} = 450°C)	0.006	0.018	0.053	0.017	0.051	0.171	14.8
4-48 (T_{H_2} = 450°C)	0.015	0.048	0.162	0.016	0.050	0.170	16.2

* Specific activity was calculated using dispersion data derived from CO chemisorption experiments.

time to 50 h (sample 4-48), which changed the proportions of the platinum species to 23% Pt_I, 24% Pt_{IC}, and 53% Pt_C, caused a significant decrease in the intensity of the low-temperature hydrogen uptake peak. The main hydrogen uptake region was between 150 and 300°C, and the maximum hydrogen uptake rate was observed at 210°C. The amount of unreadily reducible platinum species (which reduced above 300°C) was practically the same in both samples. These results are evidence that the regularities of platinum reduction are determined by the chemical composition of the metal complexes and by the complex–support binding strength. The dispersion of the resulting platinum particles also depends on these parameters (Table 4). The dispersion of supported platinum was estimated after the reduction of the samples with hydrogen at 450°C using pulsed hydrogen and carbon monoxide chemisorption techniques. When the most abundant species were the complexes bound via the ion-exchange mechanism (Pt_I), the formation of comparatively large particle took place (sample 2-01). An increase in the amount of coordinatively bound platinum complexes (sample 4-48) was favorable for the formation of smaller supported metal particles in spite of the increase in the reduction temperature. It follows from chemisorption data (Table 4) that the formation of coordinatively bound metal complexes during prolonged drying at 25°C makes it possible to obtain finely dispersed platinum without using high-temperature drying (120°C) or calcination (400°C).

The observed difference in the dispersion of platinum between samples 2-01 and 4-48 led to a difference between their hydrogenating activities. The results of our kinetic measurements are presented in Table 5. Clearly, sample 4-48, which contains hydrolyzed complexes with the average composition $PtCl_3O_3$ as a result of drying, is 2.5–3.0 times more active. However, since these samples are similar in the specific activity of platinum calculated with the dispersion taken into account and in the activation energy of hydrogenation, it can be concluded that the samples contain hydrogenation sites of the same nature and differ only in the number of these sites.

Drying at an Elevated Temperature

The samples to be examined, which contained 0.1, 0.3, or 1.0 wt % Pt, were dried in air under daylight conditions for 48 h. The drying temperature was varied in the 50–120°C range. It is clear from the electronic spectra presented in Fig. 6 that, as the platinum content is decreased, the ligand → metal charge transfer band maximum in the high-frequency region shifts to larger wavenumbers, occurring at 43000 cm^{-1} for the 1% Pt/Al_2O_3 sample and at 48000 cm^{-1} for the 0.1% Pt/Al_2O_3 sample. This observation indicates that more dramatic changes in the coordination sphere of platinum take place as a result of the replacement of chloro ligands by oxygen-containing ligands [29, 30] as the concentration of the complexes on the surface is decreased [23]. At the same time, the data presented in Fig. 6 demonstrate that, at a fixed platinum concentration, variation of the drying temperature over the 25–120°C range does not cause any noticeable changes in the electronic spectrum.

The drying temperature effect showed itself in the investigation of platinum reduction. According to TPR data for the sample containing 0.3% Pt (Fig. 5b), raising the drying temperature from 25 to 120°C caused a significant increase in the hydrogen uptake near 350°C. The increase in the proportion of unreadily reducible platinum species as a result of the predrying of the sample at 120°C may be due to the increase in the probability of the multisite coordination of the precursor. It is possible that, at the elevated drying temperature, as in the case of hydrothermal processing [22], the hydrolyzed platinum species condense to yield polynuclear hydroxo complexes. We demonstrated in our earlier study [36] that these complexes undergo reduction at a higher temperature and are likely capable of coordinatively binding to the support surface in a multisite mode.

This study has elucidated some chemical aspects of the drying process as an indispensable step in catalyst synthesis. It was demonstrated that the freshly dried samples consist largely of chlorine-rich outer-sphere complexes with the average composition $PtCl_5O$.
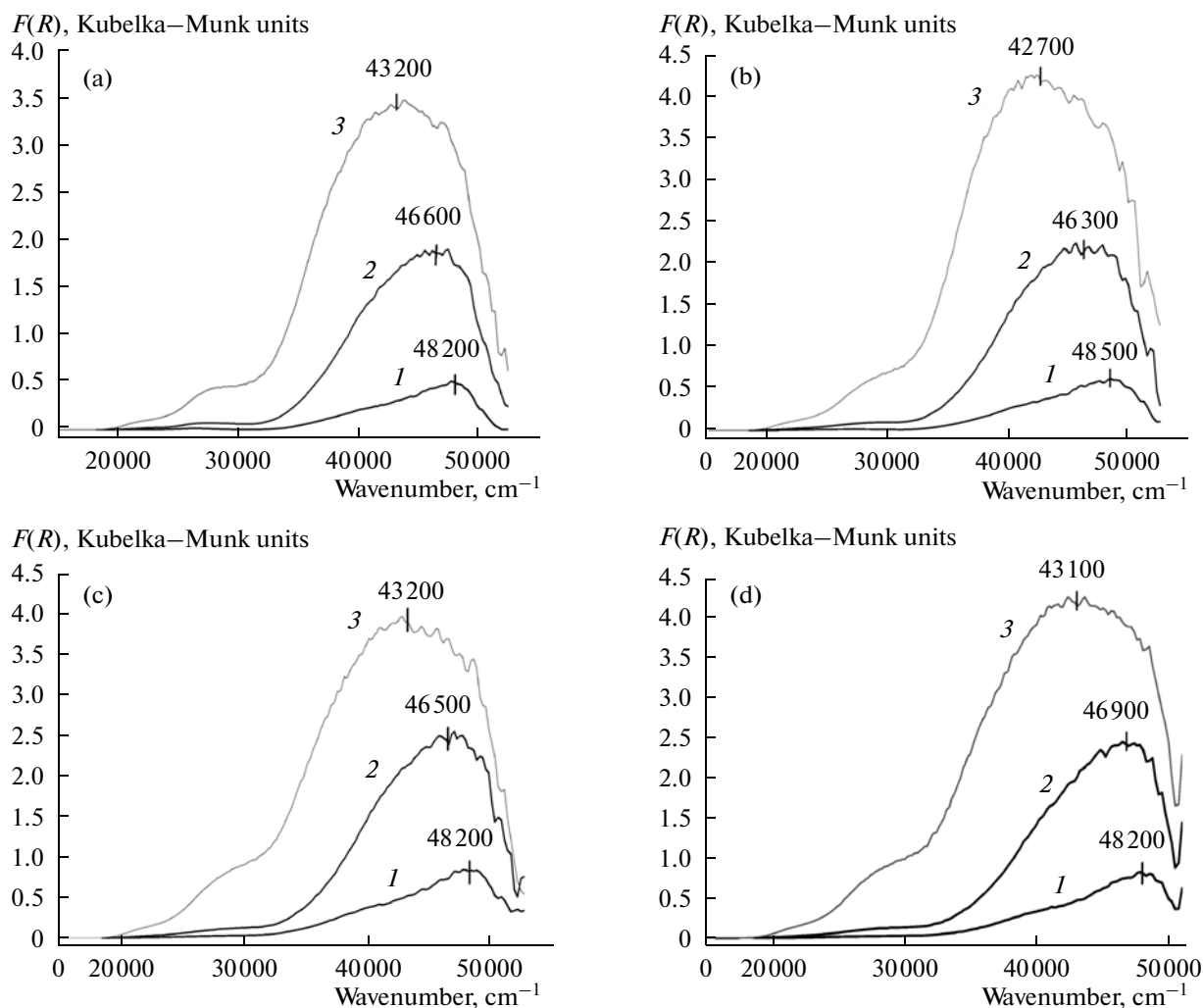
Fig. 6. Diffuse reflectance electronic spectra of the Pt(IV) complexes adsorbed on γ-Al$_2$O$_3$ for samples dried at different temperatures: (a) 25°C, (b) 50°C, (c) 100°C, and (d) 120°C. The platinum content of the samples is (*1*) 0.1, (*2*) 0.3, and (*3*) 1.0 wt %.

These complexes can be displaced from the surface by competing anions and are reducible in the temperature range from 25 to 100°C, which is characteristic of the reduction of bulk platinum chloro complexes [37]. As the drying time is extended to 50 h (25°C), the average composition of the surface complexes becomes PtCl$_3$O$_3$, the proportion of nondesorbable complex species increases to 50–60%, and the reduction temperature of these species increases as well. The reduction process yields highly dispersed particles of supported platinum, obviating the need for high-temperature drying and calcination.

Thus, after chloroplatinate is adsorbed on the alumina surface and the impregnating solution is removed, a sequence of chemical reactions involving the adsorbed metal complexes, water molecules, and surface groups of the support occurs in the adsorption layer as the sample is held at room temperature. The results of this study suggest that, as physically adsorbed water leaves the surface, favorable conditions for the

interaction of the metal complexes with surface-coordinated water molecules are established in the near-surface layer of alumina. The resulting aquated species of the complexes are capable of exchanging their ligands for surface OH groups of alumina to yield coordinatively bound complexes.

Drying at an elevated temperature (120°C) causes a marked buildup of unreadily reducible platinum species without significantly changing the extent of hydrolysis of the bound complexes. This effect may be due to the formation of polynuclear structures under these conditions as a result of the oligomerization of the hydrolyzed species of the bound platinum complexes and the formation of multisite complex–support bonds.

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REFERENCES

1. Shelimov, B.N., Lambert, J.-F., Che, M., and Didillon, B., *J. Catal.*, 1999, vol. 185, p. 462.
2. Shelimov, B.N., Lambert, J.-F., Che, M., and Didillon, B., *J. Mol. Catal. A: Chem.*, 2000, vol. 158, p. 91.
3. Spieker, W.A., Liu, J., Hao, X., Miller, J.T., Kropf, A.J., and Regalbuto, J.R., *Appl. Catal., A*, 2003, vol. 243, p. 53.
4. Regalbuto, J.R., Schrier, M., Hao, X., Spieker, W.A., Kim, J.-G., Miller, J.T., and Kropf, A.J., *Stud. Surf. Sci. Catal.*, 2002, vol. 143, p. 45.
5. Spieker, W.A. and Regalbuto, J.R., *Chem. Eng. Sci.*, 2001, vol. 56, p. 3491.
6. Spieker, W., Regalbuto, J., Rende, D., Bricker, M., and Chen, Q., *Stud. Surf. Sci. Catal.*, 2000, vol. 130A, p. 203.
7. Regalbuto, J.R., Agashe, K., Navada, A., Bricker, M.L., and Chen, Q., *Stud. Surf. Sci. Catal.*, 1998, vol. 118, p. 147.
8. Oudenhuijzen, M.K., Kooyman, P.J., Tappel, B., van Bokhoven, J.A., and Koningsberger, D.C., *J. Catal.*, 2002, vol. 205, p. 135.
9. Radivojević, D., Seshan, K., and Lefferts, L., *Stud. Surf. Sci. Catal.*, 2006, vol. 162, p. 529.
10. Prestvik, R., Moljord, K., Grande, K., and Holmen, A., *J. Catal.*, 1998, vol. 174, p. 119.
11. Ronning, M., Gjervan, T., Prestvik, R., Nicholson, D.G., and Holmen, A., *J. Catal.*, 2001, vol. 204, p. 292.
12. Hwang, C.-P. and Yeh, C.-T., *J. Mol. Catal. A: Chem.*, 1996, vol. 112, p. 295.
13. Lieske, H., Lietz, G., Spindler, H., and Volter, J., *J. Catal.*, 1983, vol. 81, p. 8.
14. Lietz, G., Lieske, H., Spindler, H., Hanke, W., and Volter, J., *J. Catal.*, 1983, vol. 81, p. 17.
15. Huizinga, T., van Grondelle, J., and Prins, R., *Appl. Catal.*, 1984, vol. 10, p. 199.
16. Foger, K., *Catal. Sci. Technol.*, 1984, vol. 6, p. 227.
17. Butt, J.B., *Appl. Catal.*, 1985, vol. 15, p. 161.
18. Campanati, M., Fornasari, G., and Vaccari, A., *Catal. Today*, 2003, vol. 77, p. 299.
19. Lambert, J.-F., Marceau, E., Shelimov, B., Lehman, J., Le Bel de Penguilly, V., Carrier, X., Boujday, S., Pernot, H., and Che, M., *Stud. Surf. Sci. Catal.*, 2000, vol. 130B, p. 1043.
20. Bel'skaya, O.B. and Duplyakin, V.K., *Russ. J. Gen. Chem.*, 2007, vol. 77, no. 12, p. 2232.
21. Bel'skaya, O.B., Karymova, R.Kh., Kochubei, D.I., and Duplyakin, V.K., *Kinet. Catal.*, 2008, vol. 49, no. 5, p. 720.
22. Bel'skaya, O.B., Karymova, R.Kh., Kochubei, D.I., and Duplyakin, V.K., *Kinet. Catal.*, 2008, vol. 49, no. 5, p. 729.
23. Bel'skaya, O.B., Maevskaya, O.V., Arbuzov, A.B., Kireeva, T.V., Duplyakin, V.K., and Likholobov, V.A., *Kinet. Catal.*, 2010, vol. 51, no. 1, p. 98.
24. Ginzburg, S.I., Gladyshevskaya, K.A., Ezerskaya, N.A., Ivonina, O.M., Prokof'eva, I.V., Fedorenko, N.V., and Fedorova, A.N., *Rukovodstvo po khimicheskomu analizu platinovykh metallov i zolota* (Guide to Chemical Analysis of Platinum-Group Metals and Gold), Moscow: Nauka, 1965.
25. Maatman, R.W., Mahaffy, P., Hoekstra, P., and Addink, C., *J. Catal.*, 1971, vol. 23, p. 105.
26. Carballo, L., Serrano, C., Wolf, E.E., and Carberry, J., *J. Catal.*, 1978, vol. 52, p. 507.
27. Freel, J., *J. Catal.*, 1972, vol. 25, p. 149.
28. Prasad, J., Murthy, K.R., and Menon, P.G., *J. Catal.*, 1978, vol. 52, p. 515.
29. Buslaeva, T.M., Umreiko, D.S., Novitskii, G.G., Sinitsyn, N.M., and Kovrikov, A.B., *Khimiya i spektroskopiya galogenidov platinovykh metallov* (Chemistry and Spectroscopy of Platinum-Group Metal Halides), Minsk: Universitetskoe, 1990.
30. *Analiticheskaya khimiya metallov platinovoi gruppy* (Analytical Chemistry of Platinum-Group Metals), Zolotov, Yu.A., Ed., Moscow: KomKniga, 2005.
31. Shelimov, B.N., Lambert, J.-F., Che, M., and Didillon, B., *J. Am. Chem. Soc.*, 1999, vol. 121, p. 545.
32. Pechenyuk, S.I., *Sorbtsionno-gidroliticheskoe osazhdenie platinovykh metallov na poverkhnosti neorganicheskikh sorbentov* (Platinum-Group Metal Deposition on the Surface of Inorganic Sorbents via Sorption and Hydrolysis), Leningrad: Nauka, 1991.
33. Emmanuel', N.M. and Knorre, D.G., *Kurs khimicheskoi kinetiki* (Chemical Kinetics), Moscow: Vysshaya Shkola, 1984.
34. Pishchevitskii, B.I., Belyaev, A.V., Shchekochikhina, R.L., and Mal'chikov, G.D., *Kinetika reaktsii zameshcheniya ligandov v kompleksnykh soedineniyakh platinovykh metallov i zolota* (Kinetics of Ligand Substitution Reactions in Coordination Compounds of Platinum-Group Metals and Gold), Novosibirsk: Nauka, 1974.
35. *Synthesis of Solid Catalysts*, de Jong, K.P., Ed., Weinheim: Wiley-VCH, 2009.
36. Bel'skaya, O.B., Drozdov, V.A., Gulyaeva, T.I., Arbuzov, A.B., Moroz, E.M., Zyuzin, D.A., Paukshtis, E.A., Larina, T.V., and Duplyakin, V.K., *Kinet. Catal.*, 2009, vol. 50, no. 6, p. 880.
37. Shubochkin, L.K., *Khimiya platinovykh i tyazhelykh metallov* (Chemistry of Platinum-Group and Heavy Metals), Moscow: Nauka, 1975.