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Genesis of the Active-Component Precursor in the Synthesis of Pt/Al_2O_3 Catalysts: I. Transformation of the $[PtCl_6]^{2-}$ Complex in the Interaction between Chloroplatinic Acid and the γ-Al_2O_3 Surface

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Abstract—Gradient elution experiments have revealed the difference between platinum complexes in terms of the strength of their interaction with the alumina surface. A considerable part (30–40%) of the supported platinum is nondesorbable via competitive ion exchange reactions or upon changes in the charge state of the support surface. The surface platinum complexes can be divided into ion-exchangeable and coordinatively fixed species according to the nature of their bonding with aluminum oxide. Combining desorption and spectroscopic methods (EXAFS and diffuse reflectance spectroscopy) has made it possible to characterize the surface complexes. The strongest metal–support interaction takes place in the fixation of hydrolyzed platinum species.

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The synthesis and investigation of platinum–alumina catalysts have a long history: there have been extensive studies of various aspects of the preparation procedure and of its effect on the catalytic properties. In addition, the platinum–alumina composition is commonly viewed as a typical representative of adsorption-type supported catalytic systems. Therefore, based on detailed studies of the formation of platinum–alumina catalysts, one can deduce both fundamental and applied generalizations (for model and commercial catalysts, respectively) whose significance goes beyond the properties of particular catalytic compositions. Although large amounts of experimental data concerning platinum–alumina catalysts have been accumulated in the scientific literature, the totality of reactions of $[PtCl_6]^{2-}$, the usual precursor of the active component, on the support surface is still understood only fragmentarily. For this reason, the approach to the preparation of the catalysts remains empirical in many respects.

This article begins a series of publications in which we will consider the chemical transformations of the active-component precursor during the preparation of the impregnating solution and in the adsorption layer of the support, using the synthesis of supported Pt/Al_2O_3 catalysts from common metal complexes as an example. Particular attention will be focused on the mechanism of the fixation of dissolved species to the support surface and on their transformation at later stages of catalyst formation.

Present-day studies give proper attention to the supporting process, in which a solution containing the platinum chloro complex is brought into contact with the surface of an oxide material. Two basic models of the interaction between a metal acido complex and the Al_2O_3 surface are discussed in the literature. The first model assumes that the anionic complexes of platinum from the impregnating solution interact electrostatically with the alumina surface, which is protonated and positively charged at low pH values. In this case, the composition and structure of the metal complexes in the solution are identical to those on the support surface:

$$\begin{aligned} &\sim 2Al\text{–}OH + 2H^+ + [PtCl_6]^{2-} \\ &\longleftrightarrow \sim 2Al\text{–}OH_2^+\text{–}[PtCl_6]^{2-}. \end{aligned} \qquad \text{(I)}$$

Platinum adsorption in a wide pH range was studied in detail for various oxide surfaces [1–4]. This process is easily describable in terms of the electrostatic adsorption mechanism [5, 6]. The main simplification used in this model is that only the doubly charged ion $[PtCl_6]^{2-}$ is considered in platinum adsorption, although the solution may contain a variety of differently charged aqua complexes at some solute concentrations and pH values [7]. This casts doubt on the correctness of applying the model to surface processes.

Spieker et al. [8] suggested a scheme of the electrostatic binding of uncharged complexes as a result of inner-sphere transformations. According to this model, even at a moderately high solution pH, platinum is

adsorbed as a doubly charged anionic complex. This complex forms from uncharged species upon their contact with the surface either by rapid H_2O–OH exchange in the coordination sphere of platinum at high pH values of the adsorption layer,

$$[PtCl_2(OH)_2(H_2O)_2]^0 \longleftrightarrow [PtCl_2(OH)_4]^{2-} + 2H^+ \quad \text{(II)}$$

or by surface protonation,

$$2Al\text{–}OH + [PtCl_2(OH)_2(H_2O)_2]^0 \longleftrightarrow 2Al\text{–}OH_2^+\text{–}[PtCl_2(OH)_4]^{2-}. \quad \text{(III)}$$

In the chemical adsorption model, platinum is fixed through a more profound interaction between the complex and the oxide surface, specifically, ligand exchange with surface groups. The leaving group may be either a chloride ion of the platinum complex or a surface hydroxo group of the support [9, 10]:

$$\sim Al\text{–}OH + [PtCl_6]^{2-} \longleftrightarrow \sim Al\text{–}[(OH)\text{–}PtCl_5]^- + Cl^-, \quad \text{(IV)}$$

$$\sim Al\text{–}OH + H_3O^+ + [PtCl_6]^{2-} \longleftrightarrow \sim Al\text{–}[Cl\text{–}PtCl_5]^- + 2H_2O. \quad \text{(V)}$$

It is essential that this mechanism allow hydroxyl ligand exchange between a partially hydrolyzed complex and a neutral or negatively charged surface:

$$\sim Al\text{–}OH + [PtCl_4(OH)_2]^{2-} \longleftrightarrow \sim Al\text{–}[(OH)\text{–}PtCl_4(OH)^-] + OH^-, \quad \text{(VI)}$$

$$\sim Al\text{–}O^- + [PtCl_4(OH)(H_2O)]^- \longleftrightarrow \sim Al\text{–}[(O)\text{–}PtCl_4(H_2O)]^- + OH^-. \quad \text{(VII)}$$

In some works [11, 12], it is deduced from variations of the ^{195}Pt NMR intensity that electrostatic binding and the formation of inner-sphere complexes with surface AlOH groups ("grafting of the precursor onto the support") can occur simultaneously. The latter process becomes irreversible as the temperature is raised to 90°C.

It is hypothesized that aluminum ions of the support are involved in the sorption of the platinum complexes [13]. The initial stage of this process is assumed to be the dissolution of a small part of aluminum oxide via its interaction with chloroplatinic acid. This is followed by the reaction between the hydrolyzed Al^{3+} cation and the $[PtCl_6]^{2-}$ anion and by the precipitation of the resulting salt onto the support surface with the formation of $\sim Al\text{–}O\text{–}Al^{2+}PtCl_6^{2-}$. However, it seems unlikely that the dissolution of the support makes a significant contribution to platinum fixation because its rate is much lower than the metal complex sorption rate [14].

There have been studies of the adsorption of Pt(II) and Pt(IV) chloro complexes on the brominated alumina surface [15, 16]. In this case, the platinum complexes are fixed solely via the coordination mechanism, specifically, the replacement of inner-sphere chloride ligands by surface Br^- ions. This ligand exchange yields surface complexes of composition $[PtCl_{6-n}Br_n]^{2-}$, where n = 1–5. Note that, according to ^{195}Pt NMR data [15], the rate of the ligand substitution reaction on the surface is much (10^3–10^5 times) higher than the rate of the same reaction in solution.

Because aqueous H_2PtCl_6 solutions contain a wide variety of metal complexes [7], which are in dynamic equilibrium, and because surface OH groups of alumina vary considerably in reactivity [17–19], a large number of reactions occur at different rates in the multicomponent impregnation medium. Therefore, there is good reason to assume the existence of adsorbed complexes hydrolyzed to different extents and the possibility that these complexes bind to the oxide support via different mechanisms.

Here, we present a detailed study of the impregnation process, in which we quantitatively differentiated between surface species of platinum on the basis of their chemical composition and structure and the nature of the bonding between the metal complexes and the alumina surface.

EXPERIMENTAL

Sample Preparation

Samples containing 2.0 wt % Pt were obtained by the chemisorption of platinum(IV) chloro complexes from aqueous solutions onto aluminum oxide. The solution-to-support volume ratio was 10. The chloroplatinic acid solutions ($5 \times 10^{-3} - 50 \times 10^{-3}$ mol/l) to be examined and to be used in the supporting of the complex were prepared from the crystal hydrate $H_2PtCl_6 \cdot 6H_2O$ (OAO Aurat, USSR Specifications TU 6-09-2026-87). The solutions were prepared and examined in the dark at 25°C. The support was γ-Al_2O_3 (Condea) with a particle size of 0.1–0.2 mm, S_{sp} = 196 m^2/g, D_{eff} = 11.1 nm, V_Σ = 0.55 cm^3, sodium content of 0.003%, and iron content of 0.021%. Texture parameters of the support were derived from nitrogen adsorption–desorption isotherms at 77.4 K using a Sorptomatic 1900 instrument.

The platinum concentrations in the solution before and after the sorption run were determined spectrophotometrically using a standard procedure [20]. The H^+ and Cl^- concentrations were determined with a Seven-Multi ion meter (Toledo).

Platinum was sorbed for 20 min. Next, the sorbent pellets were thoroughly washed with water to remove the nonchemisorbed components of the solution from the pore space of the support. In addition, one sample was prepared by incipient-wetness impregnation of chlorinated alumina with an H_2PtCl_6 solution. γ-Al_2O_3

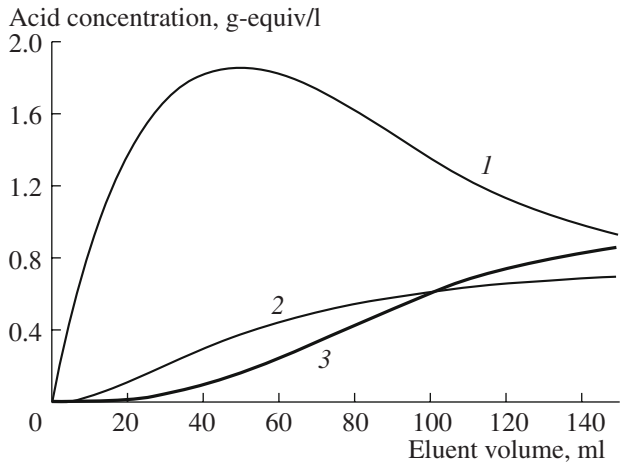

Fig. 1. Variation of the eluent composition during acid elution: (*1*) perchloric acid, (*2*) oxalic acid, and (*3*) citric acid.

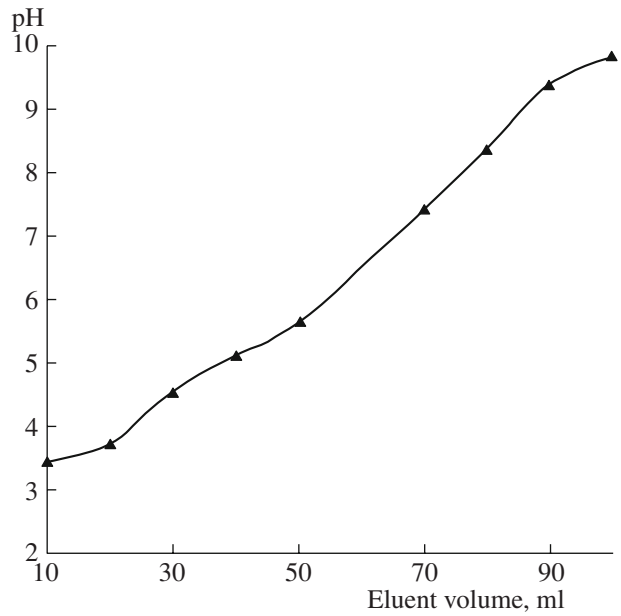

Fig. 2. Variation of the eluent pH during the desorption run.

was chlorinated with an HCl solution up to its limiting sorption capacity (0.37 (mg-equiv HCl)/g). In spectroscopic studies and desorption experiments, we used samples dried in air at 25°C for 24 h.

Sample Characterization Techniques

Gradient Elution

Acid elution. Gradient elution has found wide use in ion-exchange column chromatography [21, 22]. In this method, surface species retained by the solid support with different strengths are desorbed in sequence. We used gradient elution to reveal metal complex–support interaction effects in the fixation of platinum chloro complexes on the alumina surface. The differentiation of surface complexes was based on the principles of phase-distribution chromatography using an eluent with a progressively increasing desorbing power. The eluent was composed of perchloric (monobasic) acid (5.0 N, 50 ml), oxalic (dibasic) acid (2.0 N, 50 ml), and citric (tribasic) acid (2.0 N, 50 ml). These acids do not react with the platinum chloro complexes, do not degrade the support throughout the sorption time, and differ significantly in terms of the selectivity of sorption on alumina [23]. The eluent solution feed system ensured a gradual increase in the desorbing power of the eluent by raising the concentration of the acids entered simultaneously into the column with the sample (Fig. 1).

Metal complex desorption under a variable pH of the eluent. This technique is based on the desorption of fixed anionic complexes of platinum from the protonated alumina surface as a result of changes in the support surface charge state. The surface acidity was decreased by treating the surface with an eluent solution with a steadily increasing pH. The eluent was prepared in a special-purpose vessel by adding an alkaline agent to 200 ml of 0.2 N CH_3COOH at a rate of 1 ml/min under vigorous stirring. The pH of the solution in the vessel was monitored. The alkaline agent was a solution consisting of 1.0 N Na_2CO_3 and 0.2 N CH_3COONa. Sodium acetate was added in order to maintain a constant acetate anion concentration. This made it possible to vary the solution acidity linearly between pH 3 and pH 10 (Fig. 2). The eluent with a continuously varying acidity was continuously fed into the column with the sample.

The samples were charged into a glass column with a diameter of $D = 10$ mm and a height of $H = 400$ mm. The D/d_{pellet} ratio was 50–100. The elution rate was maintained at 1 ml/min. Under these experimental conditions, the desorption time of the complexes was determined only by the strength of their interaction with the support.

In all desorption runs, we sampled the solution leaving the column in order to determine its platinum and chloride ion contents. The total concentration of chloride ions (coordinated and free Cl^-) was measured by the Volhard method [24]. The concentration data thus obtained were used to plot desorption curves illustrating the dynamics of platinum and chlorine removal by the eluent passing through the column.

UV–Vis spectroscopy. The electronic spectra of solutions and powders were recorded on a UV-2501 PC spectrophotometer (Shimadzu) with an ISR-240A diffuse reflectance attachment. The spectra of solid samples 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 (KM units) versus wavenumber.

Table 1. Properties of the aqueous H_2PtCl_6 solutions

C_{Pt} in the solution, mmol/l	pH		C_{Cl^-}, free, mmol/l	C_{Cl^-}, total, mmol/l (calculated)	Free Cl^- fraction, %
	measured	calculated			
0.5	3.01	3.0	0.15	3.0	5.0
10.3	1.69	1.69	2.8	61.8	4.5

EXAFS spectroscopy. EXAFS spectra near the L_3 absorption edge of platinum were recorded at the EXAFS spectroscopy station of the Siberian Synchrotron Radiation Center in Novosibirsk (current of 70–90 mA in the electron booster storage ring (VEPP-3), fluorescence mode). In the separation of the oscillating component χ (k) and in the derivation structural information, we used the program VIPER. The EXAFS spectra were simulated for $k^3\chi(k)$ in the wavenumber range 2.5–11.0 Å^{-1}. The standards for the Pt–Cl and Pt–O bonds were $K_2[PtCl_6]$ and $H_2[Pt(OH)_6]$ powders, respectively. The coordination numbers determined for these bonds were normalized to the overall coordination number of 6.

The spectra of solutions were recorded in the dark because light would markedly accelerate the hydrolysis of the chloro complexes [25].

RESULTS AND DISCUSSION

Solution of the Active-Component Precursor

Obviously, for understanding the transformations of platinum complexes upon their fixation to the support, it is necessary to know for certain what the initial precursor solution is before its interaction with the oxide surface. Solutions with various H_2PtCl_6 concentrations were characterized by spectroscopic methods and ionometry. Table 1 lists some characteristics of impregnating solutions with various platinum concentrations.

The data presented in Table 1 are consistent with the facts that chloroplatinic acid is completely dissociated in aqueous solution and that the Pt(IV) chloro complex is very stable. Measuring the concentration of free, uncoordinated chloride ions appearing in the solution owing to the hydrolysis of the complex anion,

$$[PtCl_6]^{2-} + nH_2O \longleftrightarrow [PtCl_{6-n}(H_2O)_n]^{-2+n} + nCl^- \quad \text{(VIII)}$$

demonstrated that, even in dilute solutions, most of the chloride ions are in the coordination sphere of platinum and the average composition of the complexes is $[PtCl_{5.7}(H_2O)_{0.3}]^{-1.7}$. This inference is supported by spectroscopic data for the solutions.

In Fig. 3, we compare the EXAFS spectrum of an H_2PtCl_6 solution (C_{Pt} = 5 mmol/l) with the spectra of reference substances in which the coordination sphere of platinum contains only chlorine atoms ($K_2[PtCl_6]$) or only oxygen atoms ($H_2[Pt(OH)_6]$). In the spectrum of the solution examined, the strong peak is due a Pt–Cl distance of 2.32 Å with a coordination number of about 6. We simulated the first coordination sphere of platinum, assuming that it contains either only chloride ligands or both chloride and oxygen-containing ligands. Variation of the oxygen coordination number of platinum in the second model led to implausible results: either the coordination number of the central metal atom increased dramatically or negative Debye factors were obtained. The UV spectrum of a more dilute chloroplatinic acid solution (0.5 mmol/l) is shown in Fig. 4. The extent of hydrolysis of the chloro complex was estimated from the variation of the intensity of the characteristic absorption band at 38 000 cm^{-1} (chlorine-to-platinum charge transfer) in the electronic spectrum of the complex [26–28]. It is clear from Fig. 4 that the band intensities in this spectrum are only slightly different from those in the spectrum of the unhydrolyzed $[PtCl_6]^{2-}$ complex obtained by adding extra chloride ions to the solution. Thus, an analysis of spectroscopic data demonstrated that, in a wide concentration range, the H_2PtCl_6 solution may contain partially hydrolyzed species, but most of the platinum is in the form of chloroplatinate.

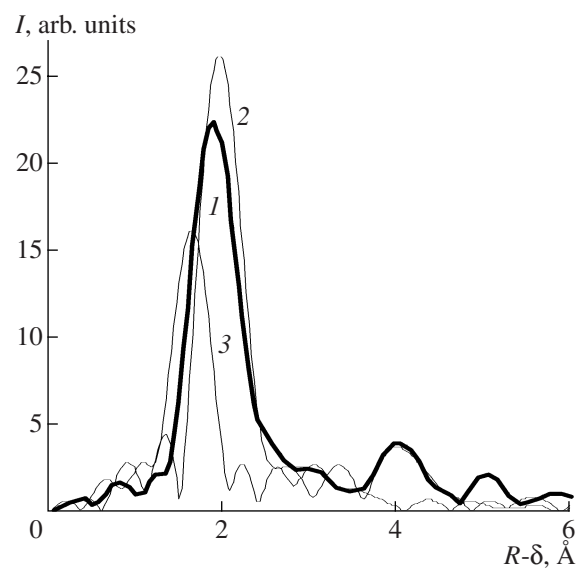

Fig. 3. EXAFS spectra of (*1*) the H_2PtCl_6 solution with C_{Pt} = 5.0 mmol/l and (*2*, *3*) model samples in which platinum is surrounded by (*2*) chlorine ($K_2[PtCl_6]$) and (*3*) oxygen ($H_2[Pt(OH)_6]$).

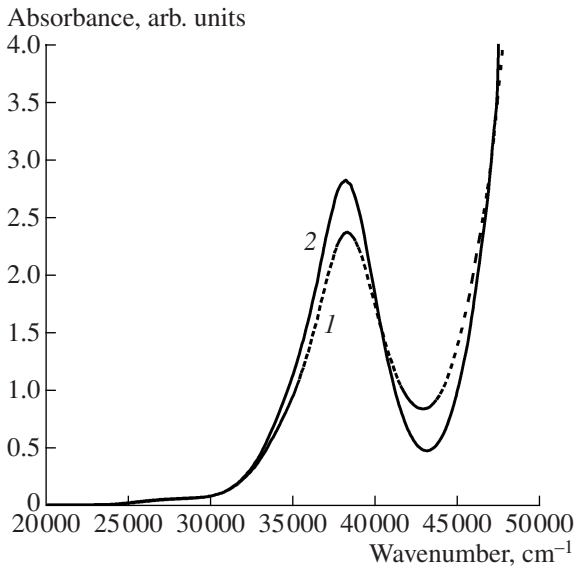

Fig. 4. Change in the electronic absorption spectrum of H_2PtCl_6 (C_{Pt} = 0.5 mmol/l) caused by partial hydrolysis: (*1*) H_2PtCl_6 solution and (*2*) H_2PtCl_6 + HCl. The decrease in absorbance at 38000 cm^{-1} (262 nm) and the increase in absorbance at 43000 cm^{-1} (230 nm) indicate the presence of platinum chlorohydroxo complexes [26].

Interaction between the Precursor and the Support Surface

During the interaction between a chloroplatinic acid solution and the alumina surface, the adsorption of the complexes is accompanied by a dramatic increase in the pH of the solution and by the appearance of extra Cl^- ions in the equilibrium solution (Table 2).

According to current views of the H_2PtCl_6 fixation mechanism [8–12], the neutralization of acid protons, which is responsible for the increase in pH, results from the interaction between the complex anion and the protonated hydroxo groups of the support and/or from anion exchange of surface OH^- groups for $[PtCl_6]^{2-}$ (reaction (I)).

The increase in the chloride ion concentration in the solution upon platinum sorption can be explained both by the hydrolysis of the adsorbed complex caused by the increasing pH of the impregnating solution,

$$\sim Al\text{–}[PtCl_6]^{2-} + H_2O \;\; \sim Al\text{–}[PtCl_5(H_2O)]^- + Cl^- \longleftrightarrow \sim Al\text{–}[PtCl_5(OH)]^{2-} + Cl^- + H^+, \quad \text{(IX)}$$

and by the replacement of Cl^- by hydroxide ligands of the support upon the fixation of part of the metal complexes via the ligand exchange mechanism (reaction (IV)).

However, knowledge of the amount of chloride ions that have passed into the solution is insufficient to judge how deep the changes in the composition of the complexes on the alumina surface are, because part of the released chloride ions can remain adsorbed on the support. Study of the adsorbed platinum complexes by EXAFS and diffuse reflectance spectroscopy demonstrated that the interaction of these complexes with the support surface causes marked changes in the coordination sphere of platinum. It follows from the EXAFS spectra (Fig. 5) that the average oxygen coordination number is 3. Due to hydrolysis proceeding to a significant extent, the charge transfer band in the electronic spectrum [26–28] is shifted to higher frequencies (Fig. 6).

The above data provide averaged information. In order to gain a more detailed insight into the surface platinum species, we carried out desorption runs in combination with spectroscopic studies.

Composition and Properties of the Surface Complexes

A possible way of investigating surface complexes is by their sequential desorption followed by separate characterization of the desorbed species in the solution and the undesorbed species on the surface.

The desorbing solutions for removal of the fixed anionic complexes of platinum were composed of acids of different basicities. As the concentration and desorbing power of the competing anion was increased (gradient elution was performed), the ion-exchangeable platinum complexes were forced out from the oxide surface into the solution in the order of how strongly these complexes interact with the protonated hydroxo groups of the surface. The high acidity of the medium prevented hydrolysis of the complexes, and the acid anions (A^{n-}) in the eluent, competing for the adsorption sites of the support, forced out the surface complexes into the solution without changing the coordination sphere of plati-

Table 2. Cl^- and H^+ concentrations in the impregnation solution before and after sorption

H_2PtCl_6 solution	Platinum concentration of 0.5 mmol/l		Platinum concentration of 10.3 mmol/l	
	[Cl^-], mmol/l	[H^+], mmol/l	[Cl^-], mmol/l	[H^+], mmol/l
Initial	0.15	0.98	2.8	20.4
Equilibrium	1.16	0.0002	4.8	0.15

Note: The volume of the solution is 25 ml, and the support weight is 2.5 g.

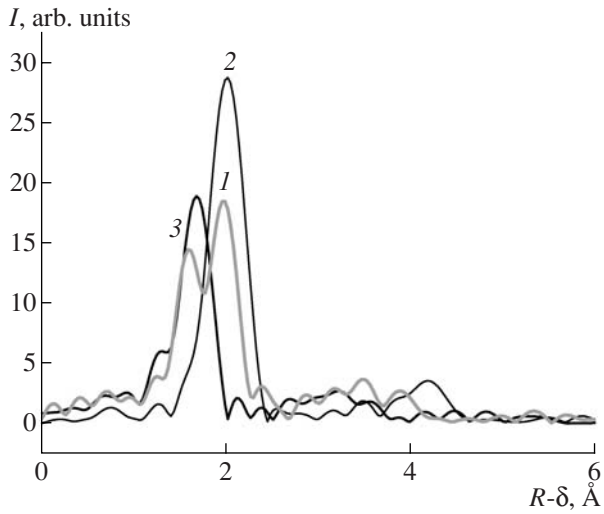

Fig. 5. Atomic radial distribution curves for (*1*) H_2PtCl_6/Al_2O_3 (2% Pt, $N(O) = N(Cl) = 3$) and for the reference compounds (*2*) $K_2[PtCl_6]$ ($N(Cl) = 6$, $R(Pt–Cl) = 2.32$ Å) and (*3*) $H_2[Pt(OH)_6]$ ($N(O) = 6$, $R(Pt–O) = 2.0$ Å).

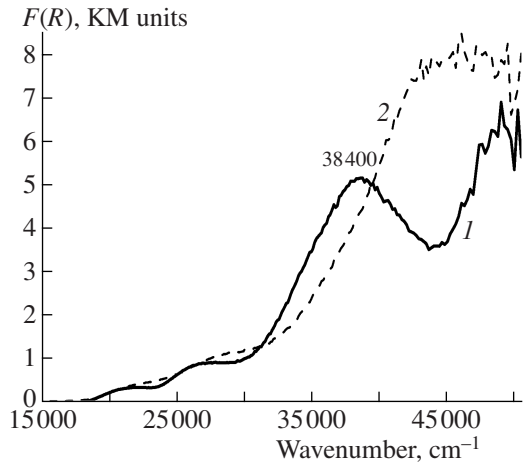

Fig. 6. Diffuse reflectance spectra of the H_2PtCl_6 complex supported on (*1*) chlorinated and (*2*) nonchlorinated Al_2O_3. The supported platinum content is 2 wt %.

num. In addition, there was desorption of adsorbed chloride ions that had resulted from the reaction between the chloroplatinate and the oxide surface:

$$\text{Al–}[\text{Pt}(\text{H}_2\text{O})_x\text{Cl}_{6-x}]_{\text{surf}} + \text{A}^{n-}_{\text{sln}} \longleftrightarrow \text{Al–A}_{\text{surf}} + [\text{Pt}(\text{H}_2\text{O})_x\text{Cl}_{6-x}]^{2-}_{\text{sln}}, \quad \text{(X)}$$

$$\text{Al–Cl}_{\text{surf}} + \text{A}^{n-}_{\text{sln}} \longleftrightarrow \text{Al–A}_{\text{surf}} + \text{Cl}^-_{\text{sln}}. \quad \text{(XI)}$$

Based on the amounts of Pt and Cl^- determined in the eluate, we constructed plots illustrating the dynamics of the removal of these components by the eluent passing through the column with the sample (Fig. 7).

The desorption profile shown in Fig. 7 indicates three platinum removal regions corresponding to different strengths of the surface complex–support interaction. Estimation of the amount of platinum desorbed in each region demonstrated that 34% of the supported platinum (or half the removed metal) is readily eluted by the first 50-ml portion of the solution consisting largely of 1.0–1.2 N perchloric acid. The two more strongly held species account for 21 and 13% of the supported platinum. At the same time, 30% of the platinum remained on the support and was irremovable under our experimental conditions.

The chloride ions are also desorbed nonuniformly. Part of them is readily removable before the beginning of platinum desorption. It is likely that these ions are not coordinated, but are formed by chloroplatinate hydrolysis and are independently adsorbed on the support. The Cl/Pt ratio in the readily desorbable complexes is close to 5, while the more strongly bound species are depleted in chlorine and are, therefore, hydrolyzed to a considerable extent. This inference is confirmed by the electronic spectra of solutions having equal platinum concentrations but falling into different regions of the desorption profile. As can be seen from Fig. 8, the intensity of the $Cl^- \longrightarrow Pt$ charge transfer band at 38000 cm^{-1} (262 nm) decreases monotonically.

The EXAFS study of the composition of the surface complexes demonstrated that, as the species weakly bound to the support are removed, the number of oxygen-containing ligands in the coordination sphere of platinum increases.

It is clear from Table 3 that, as the compounds less strongly bound to the support are removed, the average oxygen coordination number in the surface complexes increases from 3 to 4.1. Thus, the platinum fixation strength is correlated with the precursor composition. Specifically, the platinum–support interaction is stronger when the platinum complex is partially hydrolyzed. Because the O(OH) group readily forms bridged species, it is possible that polynuclear, unreadily desorbable complexes form on the surface.

According to the data presented in Table 3, the strongly bound, nondesorbable complexes have an oxygen coordination number of $N(O) = 4$ and are surface compounds of composition $[PtCl_2(OH)_4]/Al_2O_3$ and/or $[PtCl_2(H_2O)_4]/Al_2O_3$. It is likely that they interact with alumina not via the ion-exchange mechanism, but via the coordination mechanism, specifically, the replacement of ligands in the coordination sphere of platinum, with aluminum oxide acting as a macroligand:

$$\sim\text{Al–OH} + [\text{PtCl}_x(\text{OH})_y]^{2-} \longleftrightarrow \sim\text{Al–}[(\text{OH})\text{–PtCl}_{x-1}(\text{OH})_y]^- + \text{Cl}^-(\text{or OH}^-). \quad \text{(XII)}$$

If this fixation mechanism takes place, the resulting complexes will not be removed either by competitive ion exchange or as a result of a change in the surface charge.

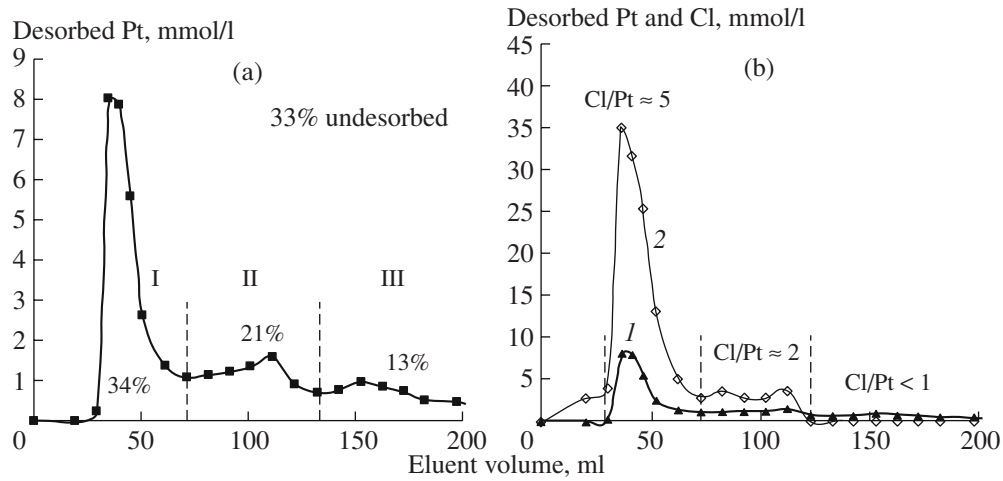

Fig. 7. (a) Results of the gradient elution of platinum compounds with acid solutions. For desorption region I, the eluent composition is 1 N $HClO_4$ + 0.1 N $C_2O_4H_2$ + 0.01 N $C_6O_7H_8$; for desorption region II, 1.8 N $HClO_4$ + 0.5 N $C_2O_4H_2$ + 0.3 N $C_6O_7H_8$; for desorption region III, 1.2 N $HClO_4$ + 0.6 N $C_2O_4H_2$ + 0.7 N $C_6O_7H_8$. (b) Variation of the amounts of desorbed (*1*) platinum and (*2*) chloride ion with an increasing desorbing power of the eluent.

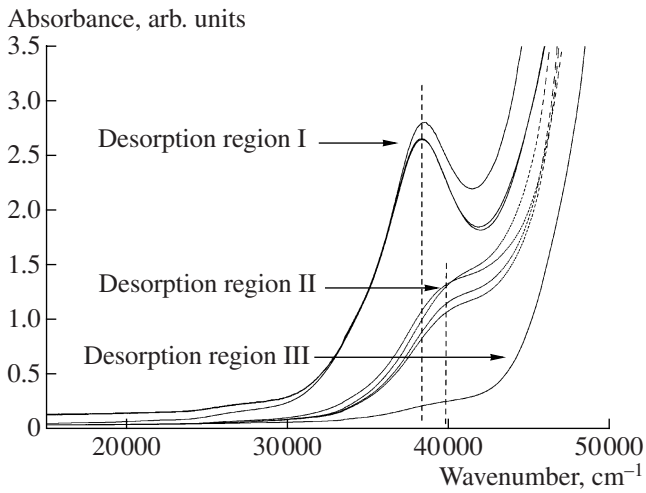

Fig. 8. Electronic absorption spectra of the solutions corresponding to the peaks in the desorption curves. For correct comparison of the spectra, all the solutions were adjusted to the concentration 0.5 mmol/l by dilution.

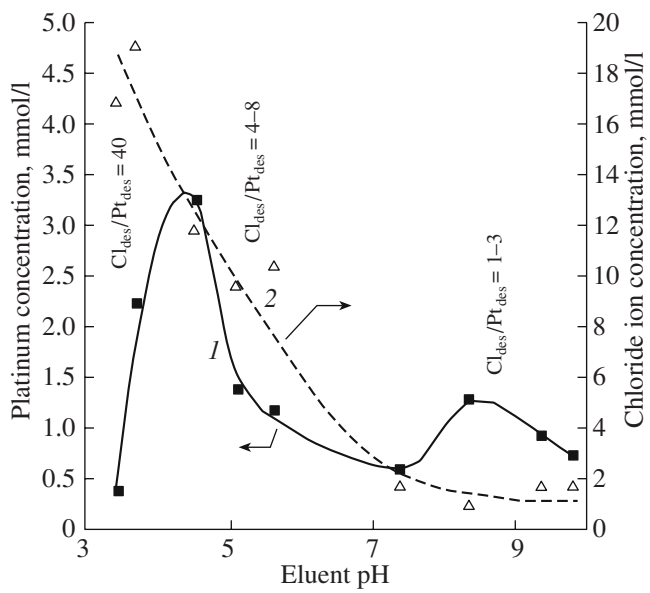

Fig. 9. Desorption of (*1*) platinum compounds and (*2*) chloride ions under eluent pH variation.

Under conditions of platinum being supported from acidic H_2PtCl_6 solutions, the surface groups of Al_2O_3 are protonated and the support is capable of adsorbing anions. By raising the pH of the solution in contact with alumina, it is possible to recharge the surface so that the support will lose its ability to hold anionic complexes. The anionic species will pass into the solution, while the nondesorbable species, whose interaction with the support is of a different nature, will remain on the surface.

Figure 9 presents the results of the desorption experiments in which the pH of the eluent was varied.

It follows from the data presented in Fig. 9 that changing the acidity of the eluent from pH 3 to pH 11 causes charged platinum-containing species to pass into the solution. In addition, considerable amounts of uncoordinated chloride ions are desorbed. These ions result from both complex fixation and from hydrolysis caused by the decreasing acidity of the eluent. The desorption profile has two platinum complex removal peaks, one in the acid region (pH 3–7) and the other in the alkali region (pH 9–11) after the point of zero charge of Al_2O_3 (pH 8.5 [4]). Thus, as in the case of acid elution, the hydrolyzed, chlorine-depleted complexes are more strongly fixed on the support and a con-

Table 3. EXAFS data for 2% Pt/γ-Al_2O_3 samples obtained by the sequential desorption of surfaces complexes

Entry	Sample	*R*(Pt–Cl)	*N*(Cl)	*R*(Pt–O)	*N*(O)
1	Initial Pt/γ-Al_2O_3	2.29	3.0	1.98	3.0
2	Pt/γ-Al_2O_3 (I): weakly bound species are desorbed	2.28	2.3	1.99	3.7
3	Pt/γ-Al_2O_3 (I) + (II): two kinds of platinum species are desorbed	2.30	2.2	2.03	3.8
4	Pt/γ-Al_2O_3 (I) + (II) + (III): surface platinum species nondesorbable by ion exchange	2.30	1.9	2.01	4.1

Note: *R*(Pt–Cl) and *R*(Pt–O) are the Pt–Cl and Pt–O bond lengths (Å), respectively; *N*(Cl) and *N*(O) are, respectively, the chlorine and oxygen coordination numbers of the Pt atom.

siderable proportion of platinum (40% of the supported metal) is in the form of nondesorbable and non-ion-exchangeable species.

It is still unclear how strongly the coordinative interaction between the metal complex and the oxide surface at the precursor fixation stage can affect the properties of the supported metal. This issue will be addressed in a forthcoming study.

CONCLUSIONS

An analysis of numerous studies devoted to the conventional synthesis of alumina–platinum catalysts suggests that there is no consensus as to the mechanisms of the surface reactions occurring in the interaction between the support and the precursor solution. In this study, we demonstrated that platinum fixation can be due to both ion exchange, in which the platinum complex does not change its nature when passing from the solution to the support surface, and coordinating interaction, in which surface groups of the support enter the coordination sphere of platinum. This coordination changes the chemical composition of the complex and the complex–surface binding strength.

Using desorption techniques, we were able to quantitatively separate the surface platinum species on the basis of the nature of their interaction with the oxide surface. It was demonstrated for the system examined that the amount of fixed platinum is 30–40% of the supported metal.

The chemical composition of the strongly fixed complexes was determined. They are hydrolyzed species with the average formula $[PtCl_2(OH)_4]/Al_2O_3$ and/or $[PtCl_2(H_2O)_4]/Al_2O_3$ and allow the replacement of hydroxyl and/or aqua ligands in the coordination sphere of platinum by surface groups of the support.

It is likely that the proportions of different surface platinum species can be varied by changing the surface properties of the support or the concentration of the supported metal or by using supporting conditions initiating chloroplatinate hydrolysis.

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