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Genesis of the Active-Component Precursor in the Synthesis of Pt/Al_2O_3 Catalysts:

II. Synthesis of Platinum Hydroxo Complexes on the Alumina Surface As Precursors of the Active Component of Pt/Al_2O_3 Catalysts

O. B. Bel'skaya[a], R. Kh. Karymova[a], D. I. Kochubei[b], and V. K. Duplyakin[a]

[a] *Institute of Hydrocarbon Processing, Siberian Branch, Russian Academy of Sciences, Omsk, 644040 Russia*
[b] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Science, Novosibirsk, 630090 Russia*
e-mail: obelska@ihcp1.oscsbras.ru

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Abstract—The thermal hydrolysis of chloroplatinate adsorbed on γ-Al_2O_3 is a possible approach to the synthesis of surface platinum hydroxo complexes as precursors to the active component of supported platinum catalysts. It is demonstrated by EXAFS and diffuse reflectance spectroscopy that the surface chloro complexes undergo deep hydrolysis under hydrothermal conditions at various processing times and temperatures. The average oxygen coordination number of platinum in these complexes is as large as 4.5. According to gradient elution data obtained using both the competitive replacement of adsorbed complex anions and variation of the charged state of the oxide surface, the resulting hydrolyzed precursor differs from the conventional chloride precursor in the nature of binding to the surface and interacts with alumina via a coordination mechanism.

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The formation mechanism of the catalytic system platinum/alumina is still a topical issue because of the importance of this composition in practical catalysis. The common precursor of the active component in this system is chloroplatinic acid, which is irreversibly sorbed on the alumina surface from acid media. The resulting Pt/Al_2O_3 catalyst has inhomogeneous platinum sites: part of the platinum is present as fine metal crystallites, and part as charged clusters chemically bound to the support (ionic platinum Pt^{σ}) [1, 2]. It is believed that these clusters are selective paraffin aromatization sites, and raising their proportion in the catalyst is considered to be a way of advancing reforming catalysts [3]. One approach to the stabilization of platinum in the ionic state under conditions of high-temperature reductive treatment of the catalyst is to use platinum hydroxo complexes as the precursor compounds. An advantage of these precursors is that they make it possible to bind the metal tightly through exchange of OH ligands of the complex for surface hydroxo groups of alumina, which serves as a kind of macroligand in this case. In addition, the capacity of the oxo and hydroxo groups of the complexes for forming bridging bonds enables one to obtain polynuclear structures and, thereby, form the active site geometry at the early stages of the synthesis.

The main obstacle to the employment of the platinum hydroxo complex $H_2[P(OH)_6]$ in catalyst preparation is its poor solubility in water. Due to its amphoterism, this compound can be used as both alkaline and acidic solutions. In the former case, there are problems arising from the introduction of undesired cations into the catalyst; in the latter case, the problem is platinum hydroxide precipitation caused by the abrupt increase in pH upon contact between the acidic solution and the oxide support surface.

Here, we suggest a new approach to obtaining platinum hydroxo complexes bound to the alumina surface. The essence of this approach is to hydrolyze the preadsorbed chloride precursor of platinum. The novelty of this approach is that the hydrolysis is carried out not by means of a change in the pH of the medium (which would introduce foreign impurities into the catalyst), but by making use of the temperature factor, specifically, by conducting hydrolysis with water above 100°C (under so-called hydrothermal conditions).

EXPERIMENTAL

Sample Preparation

H_2PtCl_6/Al_2O_3 samples containing 2.0 wt % Pt were obtained by treating alumina with an aqueous solution of chloroplatinic acid. The solution-to-support volume ratio was 10. Chloroplatinic acid solutions (5×10^{-3} mol/l) were prepared from the crystal hydrate $H_2PtCl_6 \cdot 6H_2O$ (OAO Aurat, USSR Specifications TU

Samples examined and preparation conditions

Sample	Hydrothermal processing conditions	
	time, h	temperature, °C
1. S1 (starting)	No processing	No processing
2. S2 120-6	6	120
3. S3 150-6	6	150
4. S4 190-6	6	190
5. S5 150-3	3	150
6. S6 150-12	12	150

6-09-2026-87) immediately before the synthesis. 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, a sodium content of 0.003%, and an iron content of 0.021%. The texture parameters of the support were derived from nitrogen adsorption–desorption isotherms at 77.4 K using a Sorptomatic 1900 instrument. H_2PtCl_6 was sorbed at room temperature 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. The platinum concentrations in the solution before and after the sorption run were determined spectrophotometrically using a standard procedure [4]. The H^+ and Cl^- concentrations were determined with a SevenMulti ion meter (Mettler, Toledo). In order to obtain a model system containing the unhydrolyzed complex, one sample was prepared by incipient-wetness impregnation of chlorinated alumina with an H_2PtCl_6 solution. γ-Al_2O_3 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.

The surface synthesis of platinum hydroxo complexes was carried out in titanium autoclaves with glass inserts. H_2PtCl_6/Al_2O_3 air-dried at room temperature was placed into an autoclave, and water was added (solid : liquid = 1 : 10 vol/vol). The hydrothermal synthesis temperature was varied between 120 and 190°C; the synthesis time, between 3 and 12 h. The samples thus prepared are characterized in the table.

The platinum, hydrogen ion, and chloride ion concentrations were measured in the hydrothermal medium during the synthesis. These measurements demonstrated that the resulting platinum complexes are tightly bound to the support surface: no platinum compounds passed into the aqueous phase. The highest hydrothermal synthesis temperature was set to be 190°C for the reason that raising the temperature to 200°C caused irreversible destruction of the support.

Sample Characterization Techniques

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}). Electronic diffuse reflectance spectra (DRS) were presented as the Kubelka–Munk function versus wavenumber.

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. The spectra of powders were recorded at a current of 70–90 mA in the electron booster storage ring (VEPP-3). In the separation of the oscillating component $\chi(k)$ 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 Pt–Cl and Pt–O bond standards were $K_2[PtCl_6]$ and $H_2[Pt(OH)_6]$ powders, respectively. The coordination numbers determined for these bonds were normalized to an overall coordination number of 6.

Gradient elution. In the gradient elution method, surface species retained by the solid support with different strengths are desorbed in sequence. In this study, two gradient elution variants were used, which are detailed in our previous publication [5]. In the first variant, the removal of surface complexes was due to the replacement of platinum complex anions by anions of monobasic, dibasic, and tribasic acids (A^{n-}, n = 1–3) differing significantly in terms of their sorption strength on alumina:

$$\mathrm{Al{-}[Pt(OH)_{\mathit{x}}Cl_{6-\mathit{x}}]^{2-}_{surf}} + \mathrm{A^{\mathit{n}-}_{sln}}$$
$$\longleftrightarrow \mathrm{Al{-}A^{\mathit{n}-}_{surf}} + \mathrm{[Pt(OH)_{\mathit{x}}Cl_{6-\mathit{x}}]^{2-}_{sln}}.$$

In the second variant, the desorption of the bound anionic platinum complexes was due to the changes in the support surface acidity caused by the treatment of the sample with an eluent solution with a steadily increasing pH. The continuous variation of the eluent pH was carried out by mixing 0.2 N CH_3COOH and 1.0 N Na_2CO_3 solutions.

In all desorption runs, we sampled the solution leaving the column in order to determine its platinum [4] and chloride ion [6] contents. The concentration data thus obtained were used to plot desorption curves illustrating the removal of platinum and chloride ions by the eluent passing through the column. After the desorption runs, the residual, undesorbed platinum was quantified in all samples.

RESULTS AND DISCUSSION

Thermal Hydrolysis of the Chloroplatinate Ion in Aqueous Solution

In order to study the hydrolysis-accelerating effect of the temperature factor alone, ruling out the effects of the surface groups of the support, we performed spe-

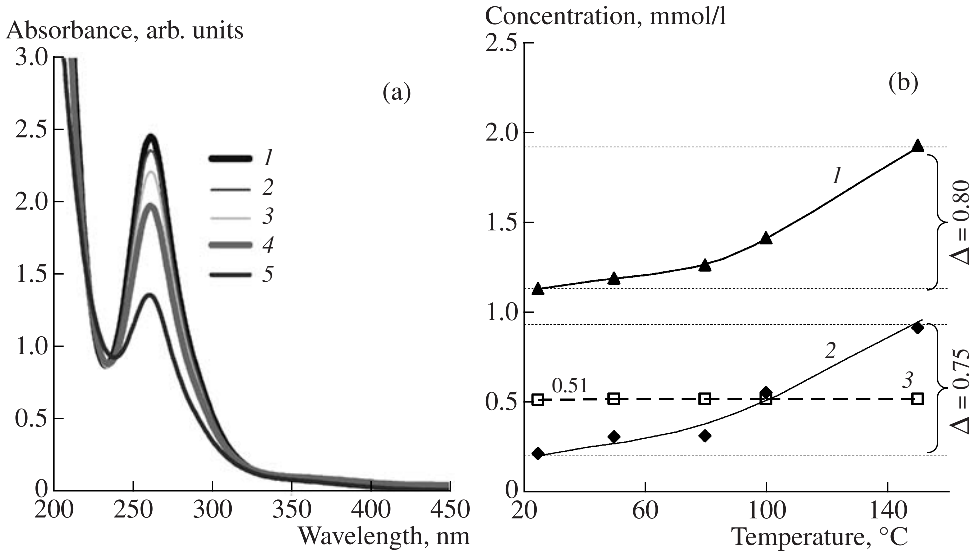

Fig. 1. Thermal hydrolysis of the chloroplatinate ion in aqueous solution: (a) electronic absorption spectra at (*1*) 25, (*2*) 50, (*3*) 80, (*4*) 100, and (*5*) 150°C; (b) evolution of the (*1*) hydrogen ion and (*2*) uncoordinated chloride ion concentrations in the aqueous $H_2[PtCl_6]$ solution and (*3*) the $C_{Pt} = 0.5$ mmol/l line.

cial-purpose experiments on aqueous solutions of chloroplatinic acid. The solutions were heat-treated in the dark at 50, 80, 100, and 150°C for 30 min. As is demonstrated in Fig. 1, the hydrolysis of the platinum chloro complexes is accompanied by a weakening of the $Cl^- \longrightarrow Pt(IV)$ charge transfer absorption band at 262 nm in the electronic spectrum and by a buildup of uncoordinated chloride ions and hydrogen ions. A significant acceleration of hydrolysis is observed above 80°C. In the case of the strongest hydrothermal processing (150°C), the calculated composition of the resulting platinum complexes in the solution is $[PtCl_4(OH)_2]^{2-}$. Thus, the thermal hydrolysis of the choroplatinate ion at 100–150°C in the aqueous solution mainly yields anionic hydroxo species, probably due to the acceleration of the replacement of coordinated chloride ions by water molecules followed by the deprotonation of the aqua ligands:

$$[PtCl_6]^{2-} + 1.5H_2O \longleftrightarrow [PtCl_{4.5}(H_2O)_{1.5}]^{0.5-}$$

$$+ 1.5Cl^- \longleftrightarrow [PtCl_{4.5}(OH)_{1.5}]^{2-} + 1.5Cl^- + 1.5H^+.$$

Synthesis of Hydroxo Complexes on the Alumina Surface

The hydrolysis of the platinum chloro complexes adsorbed on the Al_2O_3 surface was carried out under hydrothermal conditions above 100°C in an excess of the aqueous phase. Like the hydrolysis of the complexes in solution, the hydrolysis of the adsorbed chloroplatinate ion results in a buildup of hydrogen and chloride ions in the aqueous medium in contact with the sample. Throughout the processing temperature range examined, the fraction of chloride ions passing into the solution is small and does not exceed 10% of the theoretically possible fraction in the case of the total replacement of the chloride ligands by aqua or hydroxo groups. However, as distinct from the above measurements in solutions, these measurements do not allow the composition of the resulting hydrolyzed species to be calculated, because part of the hydrolysis products can bind to OH sites of the oxide support.

In order to evaluate the changes in the composition of the supported complexes caused by the hydrolysis of adsorbed chloroplatinate, the resulting samples were characterized by DRS and EXAFS spectroscopy. The electronic absorption spectra of the supported complexes are shown in Fig. 2. The electronic absorption spectrum of $[PtCl_6]^{2-}$ has been described in detail [7–9]. Some publications present spectral parameters of particular hydrolyzed platinum species in solution and on the oxide surface [10–12], but there is no information covering the electronic absorption spectra of the whole variety of platinum complexes with different extents of substitution of hydroxo and aqua groups for chloride ligands. According to spectrochemical series, the chloride ion is a weaker field ligand than the hydroxo or aqua ligand [13]. As a consequence, on passing from $[PtCl_6]^{2-}$ to $[Pt(OH)_6]^{2-}$, the absorption peaks in the electronic spectrum shift to higher frequencies (Fig. 2, curves *1*, *4*). This effect is observed for the “starting” sample S1 (Fig. 2, curve *2*), whose synthesis is accompanied by chloroplatinate hydrolysis at the sorption stage, and, even more clearly, for the samples that were subjected to thermal hydrolysis.

Detailed information about the composition of the platinum complexes on the support surface was gained by EXAFS spectroscopy. This method has been widely used in the study of various stages of the synthesis of supported catalysts, from precursor solution prepara-

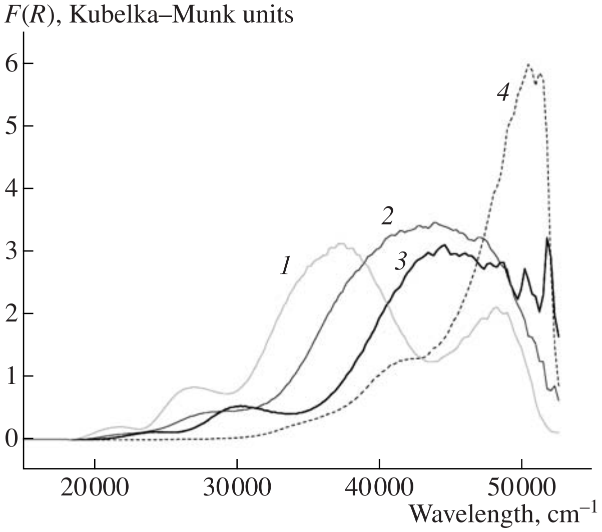

Fig. 2. Diffuse reflectance spectra of Pt(IV) complexes: (*1*) $[PtCl_6]^{2-}$ supported on prechlorinated Al_2O_3, (*2*) sample S1 (see the table), (*3*) sample S3 (see the table), and $H_2[Pt(OH)_6]/Al_2O_3$ (reference sample).

tion to the formation of final, reduced systems [14–17]. Available data demonstrate that EXAFS provides a means to determine local structure parameters (interatomic distance *R* and coordination number *N*) that are difficult to measure by other methods because of the finely divided state of the object. The EXAFS spectra presented in Fig. 3 unambiguously demonstrate that the ratio between the numbers of Pt–Cl and Pt–O bonds in the first coordination sphere of the metal changes as the hydrothermal processing conditions are made more severe. An analysis of the spectra confirmed that, in the synthesis of the "starting" sample S1, the interaction between the chloro complex and the alumina surface results in precursor hydrolysis proceeding to a significant extent: the average oxygen coordination number of platinum in the product is up to 3. This result is in agreement with earlier data demonstrating that the Pt–Cl coordination number decreases down to 2 as the complex is sorbed onto the support [16]. In the further heat treatment of the supported complex, as the hydrothermal processing temperature is raised from 120 to 150°C, oxygen atoms begin to dominate in the first coordination sphere of platinum. The oxygen coordination number reaches 4.5 at 150°C and does not increase as the temperature is further raised.

Note that the above spectra contain other, less strong bands at >2 Å, whose intensity increases with an increasing heat-treatment temperature. These bands are unassignable to stoichiometric platinum oxides and are possibly due to polynuclear complexes with Pt–O–Pt bonds or to Pt–Al distances arising from the interaction between platinum and the support. However, further investigation is required to assign these bands unambiguously.

Thus, the spectroscopic data have demonstrated that thermal hydrolysis is an efficient approach to the synthesis of hydrolyzed platinum complexes bound to the support. While hydrolysis in solution at 150°C does not go beyond the second step, hydrolysis on the surface at the same temperature proceeds to a much greater extent and yields complexes with the average composition $PtCl_{1.5}O_{4.5}$ owing to the interaction of the complexes with surface hydroxo groups of alumina.

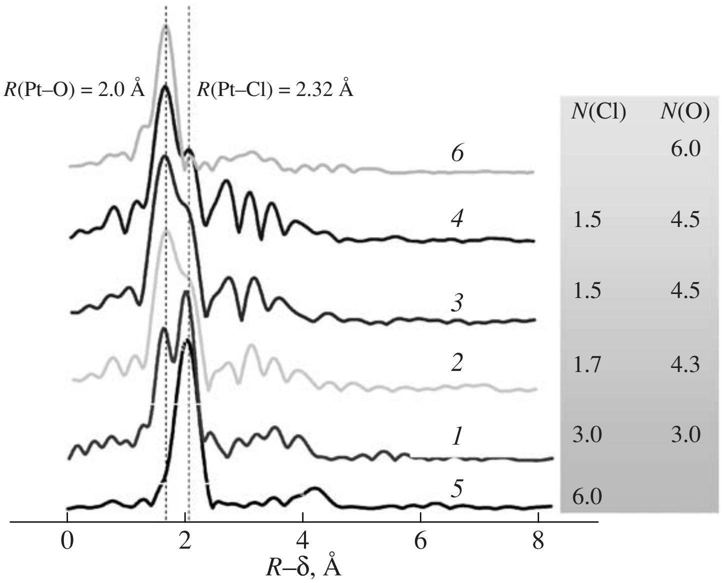

Fig. 3. EXAFS data for the samples (*1*) S1, (*2*) S2, (*3*) S3, and (*4*) S4 (see the table) and for the reference compounds (*5*) $K_2[PtCl_6]$ and (*6*) $H_2[Pt(OH)_6]$.

Interaction of Hydrolyzed Platinum Complexes with Alumina

In an earlier study [5], using desorption techniques based on the competitive sorption of anions and on variation of the alumina surface pH (gradient elution), we quantitatively divided all surface species of platinum into ion-exchangeable and coordinatively bound complexes according to the nature of their interaction with the oxide surface. The composition of these complexes was characterized by EXAFS spectroscopy. It was found that the hydrolyzed platinum complexes interact more strongly with the support. The average composition of the coordinatively bound complexes is $PtCl_2O_4$. In this study, gradient elution was used to see how strongly the changes in the composition of the supported complexes under hydrothermal conditions affect the nature of the metal complex–support interaction.

Figure 4 shows the platinum complex desorption profiles obtained for samples treated with a mixture of acids with different desorbing powers. It was demonstrated earlier [3] that the first desorption peak is due to the removal of ion-exchangeable platinum species rich in chloride ligands (weakly bound ion-exchangeable species) according to reaction (I). As the extent of hydrolysis of the fixed anionic complexes increases and it becomes increasingly possible that these complexes are held on the surface by both Coulomb and coordination bonds (tightly bound ion-exchangeable species appear), the need arises for an eluent that is adsorbed more strongly by alumina ($An2^{m-}$) (see reaction (II)). It was found that part of the platinum compounds (10–30% of their total amount) is irremovable under the desorption conditions used in our experiments and likely reacts with alumina via coordination, not ion exchange (reaction (III)).

$$\underset{\text{Weakly bound ion-exchangeable species}}{\sim\text{Al–}[\text{PtCl}_6]^{2-}_{\text{surf}}} + \text{An1}^{n-}_{\text{sln}} \longleftrightarrow \sim\text{Al–An1}^{n-}_{\text{surf}} + [\text{PtCl}_6]^{2-}_{\text{sln}}, \quad \text{(I)}$$

$$\underset{\text{Strongly bound ion-exchangeable species}}{\sim\text{Al–}[\text{PtCl}_{6-x-y}(\text{OH})_x(\text{H}_2\text{O})_y]^{n-}_{\text{surf}}} + \text{An2}^{m-}_{\text{sln}} \longleftrightarrow \sim\text{Al–An2}^{m-}_{\text{surf}} + [\text{PtCl}_{6-x-y}(\text{OH})_x(\text{H}_2\text{O})_y]^{n-}_{\text{sln}}, \quad \text{(II)}$$

$$\underset{\text{Coordinated species}}{\sim\text{Al–}[(\text{OH})\text{–PtCl}_2(\text{OH})_x(\text{H}_2\text{O})_y]^{n-}_{\text{surf}}} + \text{An2}^{m-}_{\text{sln}} \longrightarrow \text{no desorption of complexes}, \quad \text{(III)}$$

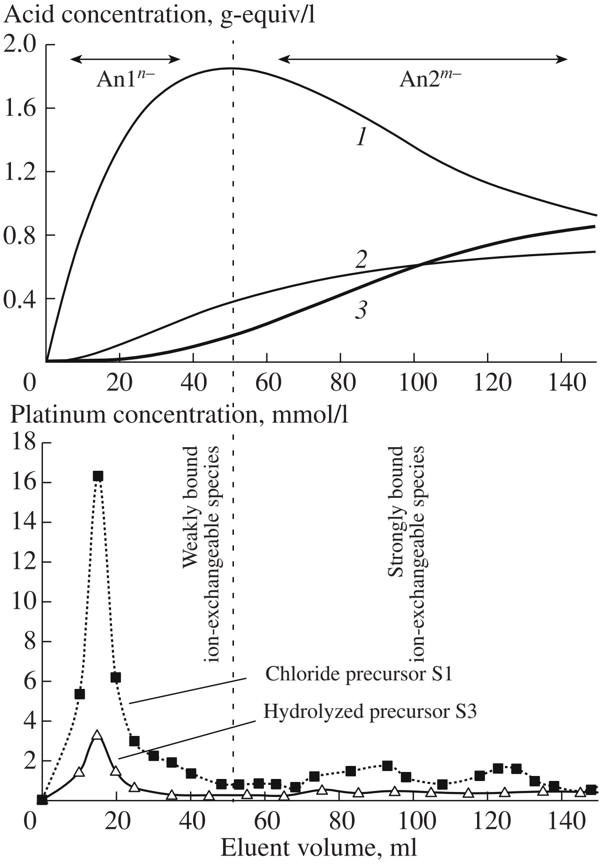

Fig. 4. Profiles of the gradient elution of the platinum compounds with acid solutions for samples SW1 and S3 (see the table): (*1*) 5.0 N perchloric acid, (*2*) 2.0 N oxalic acid, and (*3*) 2.0 N citric acid.

where $An1^{n-}$ and $An2^{m-}$ are the anions of the eluent solution that differ in the strength with which they are adsorbed by alumina ($An2^{m-} > An1^{n-}$) and force out adsorbed platinum complexes via competitive sorption.

It follows from the desorption profiles presented in Fig. 4 that the hydrothermal processing of the initial immobilized chloride precursor substantially reduces the fraction of ion-exchangeable bound platinum species. The proportion of the undesorbable complexes can be increased by increasing the processing temperature and time (Fig. 5). An analysis of the desorption data has demonstrated that, by varying hydrothermal conditions, it is possible to obtain a sample in which 80% of the initial platinum is ion-exchangeable. Note that the constancy of the complex composition in the temperature range of 150–190°C ($PtCl_{1.5}O_{4.5}$), which was established by EXAFS spectroscopy (Fig. 3), is manifested in desorption experiments as constant proportions of different platinum species on the surface.

In order to estimate the Cl_{des}/Pt_{des} ratio, we measured the chloride ion concentration in the solution leaving the column during the desorption runs (Fig. 6). In our procedure [6], the analytical amount of chlorine,

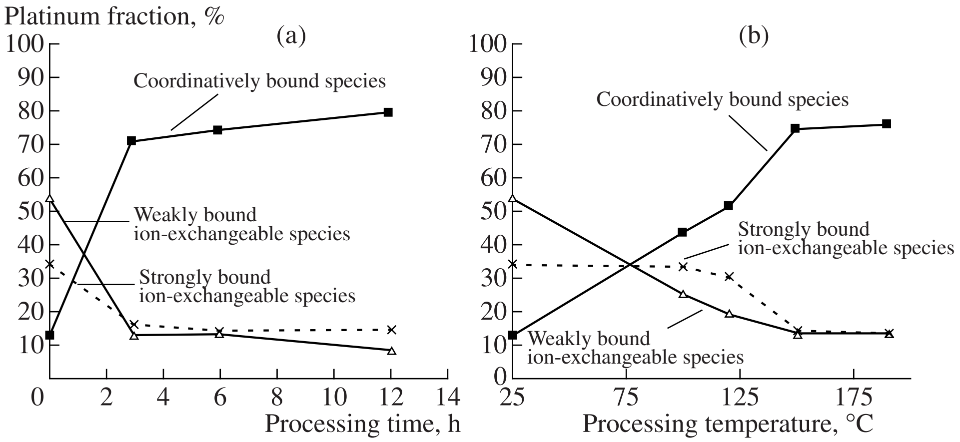

Fig. 5. Outcomes of the gradient elution of the platinum compounds with acid solutions for the "starting" sample (S1) and the samples subjected to hydrothermal processing (S2–S6) (see the table) as a function of the (a) processing time ($T = 150$°C) and (b) processing temperature ($\tau = 6$ h).

Cl_{des}, was the amount of chloride coordinated to platinum plus the amount of free (aquated) chloride that resulted from the hydrolysis of Al_2O_3-supported chloroplatinate. In the above ratio, Pt_{des} is the amount of platinum in the solution in which Cl_{des} was determined.

The Cl_{des}/Pt_{des} ratio in the starting sample at the beginning of a desorption run is close to the stoichiometric Cl/Pt ratio in the chloroplatinate ion, and it decreases on passing to strongly bound, hydrolyzed complexes. During the thermal hydrolysis of the adsorbed complexes, the resulting free chloride ions likely pass into the aqueous phase only partially and most of them remain stabilized on the support. During gradient elution, the Cl^- ions adsorbed on the alumina surface are readily removed by the first portions of the eluent and, accordingly, the desorption profile indicates a large Cl_{des}/Pt_{des} ratio.

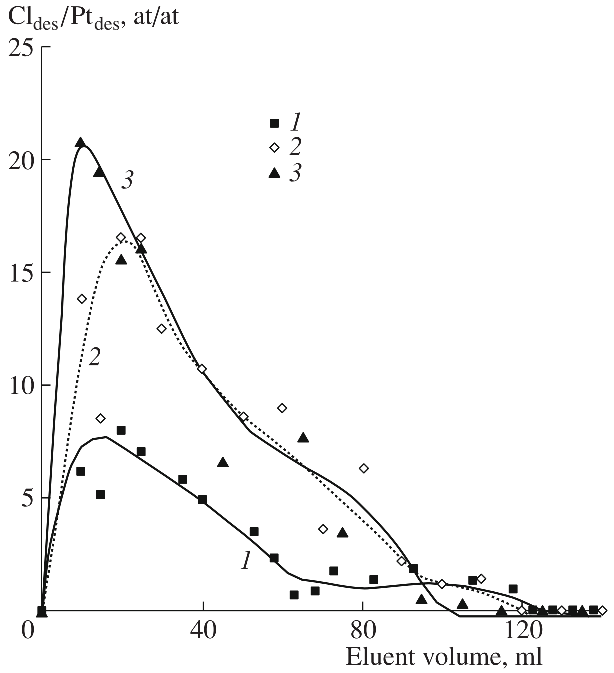

Fig. 6. Variation of the Cl_{des}/Pt_{des} ratio during the elution of the platinum compounds with acid solution for (*1*) the "starting" sample S1 and (*2*, *3*) the samples subjected to hydrothermal processing for 6 h: (*2*) S2 (120°C) and (*3*) S3 (150°C).

Figure 7 presents the results of platinum complex desorption caused by changes in the alumina surface charge. The desorption profile shows two platinum removal regions. The first occurs at low pH values and corresponds to the desorption of platinum complexes due to the competitive sorption of acetate anions, whose concentration was invariable throughout the run. In the second region, which occurs near the isoelectric point (pH 8.5), the changes in the charge state of the alumina surface cause the removal of more strongly bound anionic species of platinum. The thermal hydrolysis of the immobilized precursor causes a marked decrease in the proportion of weakly bound complexes. It is significant that, as in the case of acid elution, the fraction of undesorbable, non-ion-exchangeable species increases from 10% for the starting sample to 80% for the hydrolyzed surface complexes.

Our hypothesis that chloride and hydrolyzed platinum species interact differently with the oxide surface is confirmed by ^{195}Pt NMR data for supported platinum catalysts [18, 19]. The ^{195}Pt NMR signals from the $[PtCl_6]^{2-}$ and $[PtCl_5(OH)]^{2-}$ complexes that have resulted from chloroplatinate adsorption are similar to the signals from the chloroplatinate in solution. Therefore, aluminum oxide exerts only a weak effect on the speciation of the complex platinum anions. However, after the supported chloride complex was held at a temperature of 90°C, which accelerated hydrolysis [18], or platinum was supported as the hydroxo complex

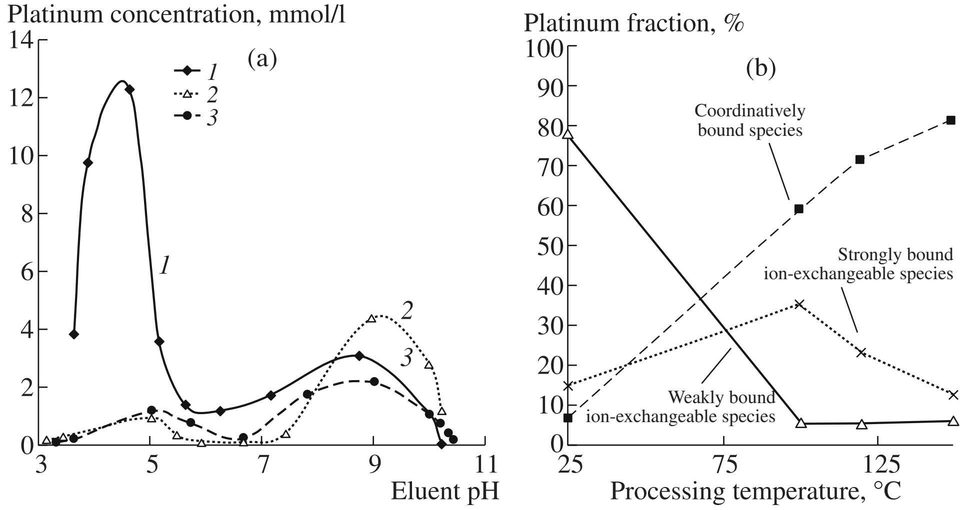

Fig. 7. (a) Results of the desorption of the platinum compounds from the alumina surface at various eluent pH values for (*1*) the "starting" sample S1 and (*2*, *3*) the samples subjected to hydrothermal processing for 6 h: (*2*) S2 (120°C) and (*3*) S3 (150°C). (b) The same at various hydrothermal processing temperatures.

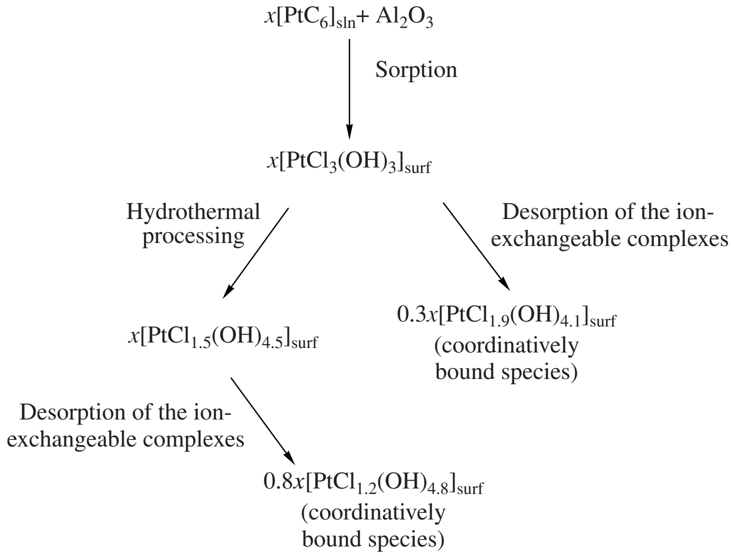

Fig. 8. Transformations of the chloroplatinate ion in its interaction with $\mathrm{Al_2O_3}$ and subsequent hydrothermal and desorption processing.

$[\mathrm{Pt(OH)_6}]^{2-}$ [19], there was no NMR signal from adsorbed species. This effect is attributed to the high chemical shift anisotropy arising from the formation of low-symmetry surface complexes via coordination with surface groups of the support:

$$\underset{\delta\mathrm{Pt}\sim 0\ \mathrm{ppm}}{\sim\mathrm{Al{-}OH_2^+}\ldots[\mathrm{PtCl_6}]^{2-}} + \mathrm{H_2O} \longleftrightarrow \underset{\text{no NMR signal}}{\sim\mathrm{Al{-}[(OH){-}PtCl_5]^-H_3O^+} + \mathrm{Cl^-}}, \tag{IV}$$

$$\underset{\delta\mathrm{Pt}\sim 650\ \mathrm{ppm}}{\sim\mathrm{Al{-}OH_2^+}\ldots[\mathrm{PtCl_5(OH)}]^{2-}} \longleftrightarrow \underset{\text{no NMR signal}}{\sim\mathrm{Al{-}[(OH){-}PtCl_5]^-} + \mathrm{H_2O}}, \tag{V}$$

$$\sim\mathrm{Al{-}OH} + \underset{\delta\mathrm{Pt}\sim 650\ \mathrm{ppm}}{[\mathrm{PtCl_5(OH)}]^{2-}} \longleftrightarrow \underset{\text{no NMR signal}}{\sim\mathrm{Al[(OH){-}PtCl_4(OH)]^-} + \mathrm{Cl^-}}. \tag{VI}$$

An EXAFS study of the thermally hydrolyzed (150°C) surface complexes before and after gradient elution demonstrated that the removal of a small amount of weakly and strongly bound ion-exchangeable species (10–20% of the total amount of platinum) affords samples containing only supported platinum compounds with an oxygen coordination number close to 5. Thus, inclusion of hydrothermal processing and/or desorption steps in the conventional catalyst preparation process (Fig. 8) is a way of obtaining samples with a hydrolyzed precursor coordinatively bound to the oxide support.

CONCLUSIONS

A new approach to the synthesis of platinum hydroxo complexes on the oxide support surface is to carry out the thermal hydrolysis of a preadsorbed chloride precursor. Hydrothermal processing at 120–150°C causes the hydrolysis of the immobilized platinum chloro complexes, yielding hydrolyzed species with the average composition $[PtCl_{1.5}(OH)_{4.5}]/Al_2O_3$ and/or $[PtCl_{1.5}(H_2O)_{4.5}]/Al_2O_3$. A correlation is established between the chemical composition of the surface complexes and the nature of their interaction with the oxide support.

The effect of the properties of the hydrolyzed precursor on the formation of platinum sites in the catalyst and on its adsorption and catalytic characteristics will be the subject of a forthcoming publication.

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