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Transformations of a Metal Complex Precursor of the Active Component in the Preparation of Pt/Al_2O_3 Catalysts

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Abstract

By the example of the formation of Pt/Al_2O_3 catalytic system an influence was demonstrated exerted by the sequence of metal complex precursor transformations at the initial stages of catalyst preparation upon the state of platinum on the active surface of the finished catalyst. Views are expounded concerning the nature of the chemical bond between the metal complex and the carrier. Approaches are considered with respect to the quantitative differentiation of ion-exchange (outer-sphere), and coordinationally bonded (inner-sphere) adsorbed metal complex species, with respect to determining their chemical composition, as well as with respect to obtaining catalysts from a deposited precursor homogeneous in the type of interaction with the carrier.

Key words: aluminium oxide-platinum catalysts, platinum chloride complexes, hydrolysis, adsorption

INTRODUCTION

Aluminium oxide-platinum catalysts are among the most demanded catalytic systems during many decades, which catalysts are widely used in oil refining, petroleum chemistry, as well as in the process of the neutralization of gas emissions. Despite a great amount of the experimental material presented in the scientific literature devoted to studying the state of the traditional precursor of the active component $[PtCl_6]^{2-}$ in aqueous solutions and its interaction with the surface of aluminium oxide, the complex of reactions on the carrier surface is rather fragmentarily studied by now. Research results known to date, especially concerning the initial stages of preparing the catalysts, are generally of qualitative character to indicate poorly controlled precursor transformations. For this reason, the approach to the preparation of Pt/Al_2O_3 type catalysts remains empirical to a considerable extent. At the same time the aluminium oxide-platinum composition is often considered a model system as a typical representative of supported catalyst systems of the adsorption type. In this connection, basing on a detailed study on the formation of aluminium oxide-platinum catalysts one could reveal the generalizations both of fundamental and of applied character, whose values are beyond the scope of a particular catalyst system.

The usual procedure of preparing the mentioned type of catalysts involves the stage of adsorbing an active component from an aqueous solution of the transition metal complex onto the surface of a carrier, followed by drying, calcination and reducing the sample. In the consideration of the present multistage scheme of the synthesis, discussions inevitably arise concerning the importance and usefulness of any detailed studies concerning the processes at each stage of the synthesis. In particular, it is believed that the investigation of the initial stages those involve the transformation of metal complex precursors in aqueous solution and on the surface of aluminium oxide under sorption interaction, offers rather little practical value. This opinion is connected with the fact that a high-temperature treatment process used for the preparation of catalysts brings the system to certain equilibrium, regardless of the “past history”. Perhaps, this assertion is true in some cases, but it is not true in general. In this paper we considered within the framework of a typical adsorption system such as $H_2PtCl_6-Al_2O_3$ the sequence of the metal complex precursor transformations in solution and on the surface of aluminium oxide at the initial stages of preparing the catalysts, proposed approaches to the differentiation of mechanisms responsible for fixing the metal complex on the carrier, as well as demonstrated the role of the precursor molecular design and of the nature of bonding with the carrier in the formation and properties of an active component.

STATE OF PLATINUM CHLORIDE COMPLEXES IN AQUEOUS SOLUTIONS

Transition metal complexes are often used as the precursors of active metal compounds for the preparation of supported catalysts. In the case of aluminium oxide-platinum catalysts such a complex precursor is traditionally represented by chloroplatinic acid $H_2[PtCl_6]$. It is important that the chemical composition of these complexes in solution, their level of approaching to the thermodynamic equilibrium and their charge state determine to a considerable extent the nature of further sorption processes. Consequently, in order to understand the processes occurring at the first stage of the catalyst preparation (the interaction between the carrier with an aqueous solution of the metal complex) there should be information available concerning the chemical reactions those occur in the course of dissolving $H_2[PtCl_6]$, as well as the factors those could affect the state of the complexes in solution.

Traditionally, the three main models of chloroplatinate hydrolysis are under consideration outlined in the papers by Miolati [1], Scilly [2] and Knozinger [3]. The earliest of these proposes that there is the a reaction with only one type of exchange such as replacing chloride ligands by hydroxide ions and does not take into account the possibility of forming aquated species as well as the presence of complex ions with charge equal to 2–. The model by Knozinger [3] is based on the assumption that $H_2[PtCl_6]$ is able of replacing only two chloride ligands by the aqua or hydroxy groups. The authors of [2] consider the $H_2[PtCl_6]$ as a strong dibasic acid, but they also suppose the ability of its hydrolysis to be limited by two stages, which, to all appearance, could be explained by the use of relatively concentrated solutions in a wide enough range of pH values. Later the views concerning the processes occurring in aqueous solutions of these complexes were developed in the studies [4, 5], using the capabilities of the methods of EXAFS and ^{195}Pt NMR spectroscopy. Some of the mentioned papers, along with the studies on the thermodynamic and kinetic aspects of ligand exchange reactions in the chloride complexes of platinum (IV), were devoted to considering various factors those accelerate the hydrolysis of the complexes in solution. Among them one should distinguish temperature [6, 7], exposure to light [8, 9], introducing a catalyzing component into the solution [10–12], for example, Pt(II) complexes [10, 12].

From the viewpoint of catalyst preparation it is important to perform the studies on the chemical reactions of Pt(IV) chloride complexes in the impregnation solutions within a wide range of platinum concentrations, those are commonly used for the preparation of model and industrially important catalysts. Thus, the authors of [13] studied the aqueous solutions of $H_2[PtCl_6]$ within the concentration range of 0.5–10.3 mmol/L. Basing on the measurement of the concentration of hydrogen ions and free uncoordinated chloride ions those emerge in the solution resulting from the hydrolysis of the complex anion, as well as on the analysis of data obtained from EXAFS and UV spectra of the solutions it was found that even for dilute solutions one can observe a prevailing amount of chloride ions to be located within the coordination sphere of platinum, whereas the average composition of the complexes corresponds to the formula $[PtCl_{5.7}(H_2O)_{0.3}]^{1.7-}$. However, even a simple exposing the solutions to natural light could exhibit a significant impact on the chemical composition of the platinum complexes [14]. The hydrolysis of the complexes could observed from decreasing the intensity of the characteristic charge transfer band (c.t.b.) inherent in chlorine-platinum charge transfer (262 nm, 38 000 cm^{-1}) in the electronic spectrum of $[PtCl_6]^{2-}$ [12,

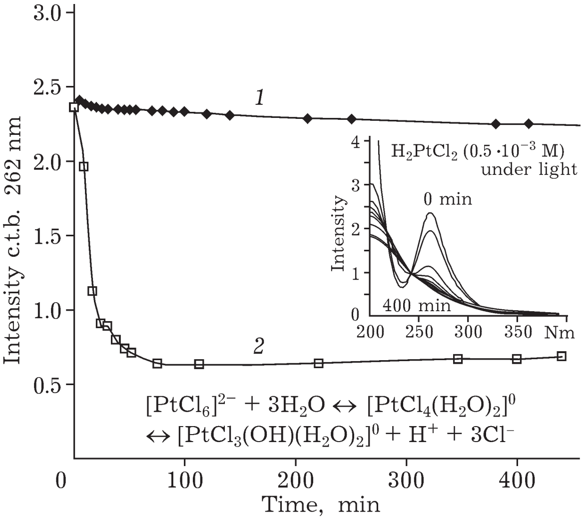

Fig. 1. Comparison of the hydrolysis dynamics of $H_2[PtCl_6]$ solution (C_{Pt} = 0.5 mmol/L) in the dark (*1*) and under light exposure (*2*) basing on changing the intensity of the characteristic absorption band at 262 nm (38 000 cm^{-1}) in the electronic spectrum of the complex [14].

15] (Fig. 1). A simultaneous measurement of proton concentration and free chloride ions in the solution allowed us to determine an average composition of hydrolyzed species. So, the solution exposure to light during 5 h resulted in the formation of mixed chloro-aqua-hydroxo complexes of predicted composition $[PtCl_3(OH)(H_2O)_2]^0$ with the charge close to zero.

Of not less urgency is also the question concerning the effect of temperature on the hydrolysis of the complexes since in the course of synthesizing supported catalysts, when the precursor solution is localized in the pore space of the carrier and an increase in the temperature is required to remove the solvent from the pores (especially from meso- and micropores), the metal complex is under hydrothermal conditions. According to the experimental results of [16], where the heat treatment of chloroplatinic acid solutions ($0.5 \cdot 10^{-3}$ M) was performed with no access of light within the temperature range of 50–150 °C, it was found that the thermal impact to a considerable extent accelerates the process of hydrolysis, especially at the temperature values higher than 80 °C.

It should be noted that, under these conditions, there occurred preferential formation of anionic hydroxo species $[PtCl_4(OH)_2]^{2-}$, to all appearance, as the result of accelerating the stage of aqua ligands deprotonation [16].

It was found that under hydrothermal conditions there is possibility of a considerable making chloroplatinate hydrolysis more profound when palladium (II) chloride complex added to the solution [17]. With the simultaneous presence of the metal complexes the hydrolysis of the labile palladium complex decelerated (the intensity of the characteristic c. t. b. at 237 nm [15] was almost unchanged). At the same time, there was a much more profound hydrolysis of chloroplatinate observed up to the formation of insoluble hydroxo complex. The electronic absorption spectra demonstrated a decrease in the intensity of the absorption band inherent in chloroplatinate (c.t.b. at 262 nm), whereas for the solution with a constant concentration of palladium, the platinum concentration was almost twice decreased. To all appearance, the action of temperature accelerates the ligand exchange in the complexes to result in the fact that the migration of chloride ligands from the tetravalent platinum complex to the divalent palladium complex with the formation of platinum (IV) aqua complexes becomes possible [17].

Thus, the preliminary investigation of the impregnating solution $H_2[PtCl_6]$ allows one to quantitatively evaluate the basic chemical reactions those occur with Pt(IV) chloride complexes, as well as to determine the intensity of influencing the process of hydrolysis by the most important factors such as the concentration of chloroplatinate, light, temperature, the presence of a more labile metal complex. The laws obtained make it possible to monitor and control the processes of the transformation of metal complexes in aqueous solution for a justified, not an empirical choice of the conditions for their attaching to the carrier at the stage of impregnation.

COMPOSITION OF FIXED PLATINUM COMPLEXES AND THE NATURE OF THEIR INTERACTIONS WITH THE CARRIER

A detailed systematization of metal complex fixation techniques in the course synthesizing catalysts from the standpoint of processes occurring therein was presented in a recent review [18]. Despite the variety of ways to fix the precursor, the analysis of the nature of the interaction between the metal complex and the carrier, two extreme cases are as a rule considered such as non-specific adsorption (the electrostatic nature of interaction) and specific adsorption (the formation of inner-sphere surface complexes). The prevailing realization of either type of interaction depends both on the nature of the synthesis of both participants of the synthesis, and on the application conditions. The most important parameters are presented by pH, metal complex concentration, solution ionic strength, impregnation temperature and time. There is no doubt that the determination of the nature of the interaction between the metal complex and the carrier is very important in order to predict the further behaviour of the catalytic system. Thus, the formation of coordinationally bonded inner-sphere complexes at the stage of fixing the precursor should result in a strong interaction between the metal complex and the carrier with the formation of highly dispersed catalysts.

The traditional analysis of interaction between a metal complex solution and a carrier in the course of synthesizing a catalyst involves monitoring the concentration of an active metal in the solution before and after sorption, the acidity of medium, as well as the emergence of possible transformation products precursor compounds, for example, due to hydrolysis in the impregnation solution. So, the interaction between the solution of $H_2[PtCl_6]$ and the surface of aluminium oxide results in the fact that the adsorption of the complexes is accompanied by an abrupt increase in the pH value of the solution with appearing additional Cl ions in the equilibrium solution [13]. According to the existing concepts [19–24] concerning the mechanisms of fixing $H_2[PtCl_6]$, the neutralization of protons resulting in increasing the pH value of solution occurs due to their interaction with the carrier hydroxyl groups, whereas the increase in the concentration of chloride ions in the solution after the adsorption of platinum could be explained both by the hydrolysis of the adsorbed complex with increasing the pH value of the impregnating solution, and by displacing Cl^- by the hydroxide ligands involved belonging to the carrier.

The investigation of the adsorbed platinum complexes using the methods of EXAFS and ESDO demonstrated that the interaction with the surface of the carrier results in a significant changing of the coordination sphere of platinum. According to EXAFS data, the average coordination number with respect to oxygen is equal to 3 [13]. In this case the electronic spectra of platinum complexes exhibited a shift of the charge transfer band towards a high-frequency region, which also indicates an increase in the number of oxygen-containing ligands in the coordination sphere of platinum [12, 15].

The results obtained with the use of physical methods demonstrate an averaged picture. In order to clarify the issue as to what an extent the adsorbed complexes are uniform in the chemical composition and in the nature of their interaction with the carrier, we proposed an approach with the use of a successive desorption of surface complexes and subsequent separate investigation of desorbed species in solution (by means of electron spectroscopy, ionometry) and non-desorbed species on the surface (ESDO, EXAFS methods) [13]. Thus, the removal of surface species of platinum attached to the protonated aluminium oxide surface in the form of anionic complexes by electrostatic interactions could be possible in the course of occurring the surface charge exchange process. In that case, a gradual increase in the eluent pH up to the values exceeding the value inherent in the zero charge point of the surface could result in the desorption of platinum anionic complexes [13]. The authors of [13, 16, 25] also used another method: the transfer of platinum anionic complexes from the surface to the solution occurred at under the competitive adsorption of specially chosen anions. The desorbing solution composition was formed from the acids of different basicity. In the process of increasing the concentration and the desorbing power of competing anions (gradient elution) there was achieved a gradual replacement of platinum complexes exhibiting an “ion exchange” nature. A high created acidity of the medium prevented the complexes from hydrolysis, whereas an anionic part of the acids contained in the eluting solution (A^{n-}), being in the competition for carrier adsorption sites, displaced the surface complexes into the solution without any changes in the coordination sphere of platinum:

$$\mathrm{Al}-[\mathrm{Pt(H_2O)}_x\mathrm{Cl}_{6-x}]_{\mathrm{surf}}+\mathrm{A}^{n-}_{\mathrm{sol}}$$

$$\leftrightarrow \mathrm{Al}-\mathrm{A}_{\mathrm{surf}}+[\mathrm{Pt(H_2O)}_x\mathrm{Cl}_{6-x}]^{2-}_{\mathrm{sol}}$$

It was found that regardless of the desorption technique used (elution with changing the eluent pH, acidic elution) a part of the platinum species fixed (close in quantity) was not removed from the surface of aluminium oxide [13]. To all appearance, their interaction with aluminium oxide did not occur according to the ion-exchange mechanism but it occurred through coordination one with replacing the ligands within the coordination sphere of platinum, whereas aluminium oxide acted as a macroligand. The analysis of the desorption profiles obtained (Fig. 2) allowed us not only to distinguish the regions of platinum removal corresponding the desorption of the complexes with different bond strength adsorbed on the surface of the carrier, but also to divide quantitatively desorbable ion-exchange platinum species and non-desorbable coordinationally bound species of platinum.

The investigation of the eluates by means of electron spectroscopy and ionometry it was found that the Cl/Pt ratio inherent in readily desorbed complexes is close to 5, whereas the more tightly bound species are hydrolyzed to a considerable extent. Determining the composition of the complexes on the surface of the carrier, performed by means of EXAFS [13] also demonstrated that as the species weakly bound with carrier removed, the number of oxygen-containing ligands in the coordination sphere of platinum increases. In this case, the coordination number with respect to oxygen N(O) for non-desorbable coordinationally bonded complexes was equal to 4, whereas the complexes themselves represented surface compounds $\mathrm{PtCl_2O_4}$.

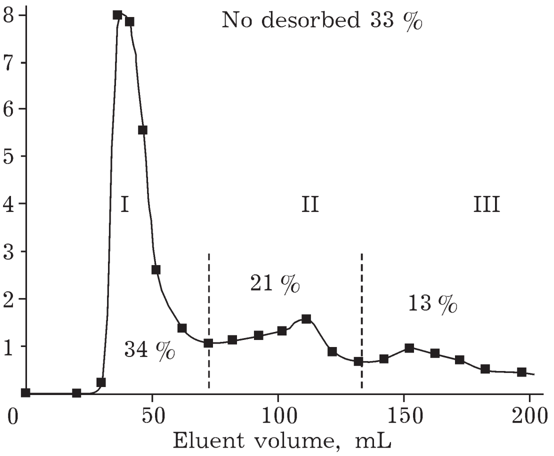

Fig. 2. Results of the gradient elution of platinum chloride by the solutions of oxalic acid and citric acid: changing the amount of platinum desorbed with increasing the eluent strength [13] (before the desorption experiments the sample was dried at 25 °C during 48 h): I–III – desorption regions, the composition of the eluent (I – 1 M $\mathrm{HClO_4}$ + 0.1 M $\mathrm{C_2O_4H_2}$ + 0.01 M $\mathrm{C_6O_7H_8}$, II – 1.8 M $\mathrm{HClO_4}$ + 0.5 N $\mathrm{C_2O_4H_2}$ + 0.3 N $\mathrm{C_6O_7H_8}$, III – 1.2 M $\mathrm{HClO_4}$ + 0.6 N $\mathrm{C_2O_4H_2}$ + 0.7 N $\mathrm{C_6O_7H_8}$).

The studies performed allowed the authors of [13, 16, 25] to propose the following scheme of reactions in the process of fixing the metal complexes on the surface of aluminum oxide:

$$\mathrm{{\sim}Al{-}2OH} + 2\mathrm{H^+} + [\mathrm{PtCl_6}]^{2-}$$

$$\downarrow \mathbf{1}$$

$$[\mathrm{{\sim}Al{-}2OH_2}]^+{-}[\mathrm{PtCl_6}]^{2-}$$

$$\downarrow \mathbf{2}$$

$$\mathrm{{\sim}Al{-}[{-}(OH)_2{-}PtCl_4]} + 2\mathrm{Cl^-} + 2\mathrm{H^+}$$

$$\downarrow \mathbf{3}$$

$$\mathrm{{\sim}Al{-}[{-}(OH)_4{-}PtCl_2]} + \mathrm{{\sim}Al{-}2Cl} + 2\mathrm{Cl^-} + 2\mathrm{H^+}$$

where ~Al–OH is the surface of aluminium oxide.

Reaction **1** represents a rapid electrostatic adsorption accompanied by an abrupt decreasing the pH value, which reaction does not result in changing the chemical composition of the fixed metal complex. Reaction **2** results in a partial replacement of the chloride ligands of $[\mathrm{PtCl_6}]^{2-}$ complex by the surface groups of the carrier: a more strongly bound complex $[\mathrm{PtCl_4(OH)_2}]$ is formed that can be desorbed only by the action of two- and tribasic competitor acids. The non-desorbable species (reaction **3**) represents the product of the further metal complex transformation in the adsorbed layer: there is a profound hydrolysis of chloroplatinate (coordination number $N(\mathrm{O}) = 4$), to all appearance, with the participation of the most basic OH groups of the carrier resulting in the formation of inner-sphere complexes.

The method of temperature programmed reduction (TPR) demonstrated that an increase in the hydrolysis level of the adsorbed complexes and in the strength of their interaction with the carrier results in increasing the temperature of their reduction. Thereby non-desorbable platinum species were reduced at the temperature values higher than 300 °C. Thus, *via* removing the desorbable species of platinum, it is possible to obtain samples with uniform precursor fixing through the coordination bond.

The heterogeneity in the nature of the interaction between the adsorbed species of platinum and the surface of the carrier is, to all appearance, connected not only with the differences in the chemical composition of adsorbed complexes, but also with the heterogeneity of adsorption sites on the surface of aluminium oxide. It is known that the hydroxyl groups on the surface of aluminium oxide exhibit different acidic properties [26–34]. Thus, the bridging OH groups are much stronger Brönsted acidic sites as compared to the terminal hydroxyl groups. The most basic is the OH group associated with octahedral and pentahedral aluminium. For example, it was demonstrated for γ-Al_2O_3 [31] that the more basic terminal OH groups those, to all appearance, are to a greater extent capable of exchanging with metal complex ligands amount to less than 30 % of total surface groups.

In the case of a fixed amount of adsorption sites on the oxide surface capable of binding to the metal complex through the coordination bond, the number of non-desorbable platinum complexes should also have a limiting value for the mentioned carrier. Indeed, *via* varying the mass fraction of platinum from 0.1 to 2.5 % it was found [25] that in the samples with low Pt content this metal is mainly present in the form of non-desorbable coordinationally bonded complexes. In this case the absolute amount of coordinationally fixed platinum species increased with the total metal content in the sample up to 1.0 % and almost did not change with further increasing the surface concentration of the metal complexes (Fig. 3). The dependence type corresponded to the Langmuir equation, and the maximum amount of coordinationally fixed platinum in the sample was equal to 0.6 mass %.

In order to increase the content of the coordinationally fixed complex species it is efficient to use thermal hydrolysis of an adsorbed chloride precursor, which, to all appearance, not only accelerates the hydrolysis of chloride complexes, but also activates an additional amount of OH groups on the carrier surface [16]. The changes in the composition of applied complexes resulting from the hydrolysis of the adsorbed chloroplatinate were registered using the methods of ESDO and EXAFS. The analysis of the EXAFS spectra (Fig. 4) demonstrated that the thermal influence upon the fixed complex resulted in the fact that oxygen atoms prevail within the first coordination sphere of platinum. So, at 150 °C the coordination number with respect to oxygen was equal to 4.5, whereas further increasing the temperature did not result in its growth. With the help of the desorption experiments, it was found that with varying the conditions of hydrothermal action, one could obtain up to 80 % of non-ion-exchange platinum species ($PtCl_{1.5}O_{4.5}$) [16].

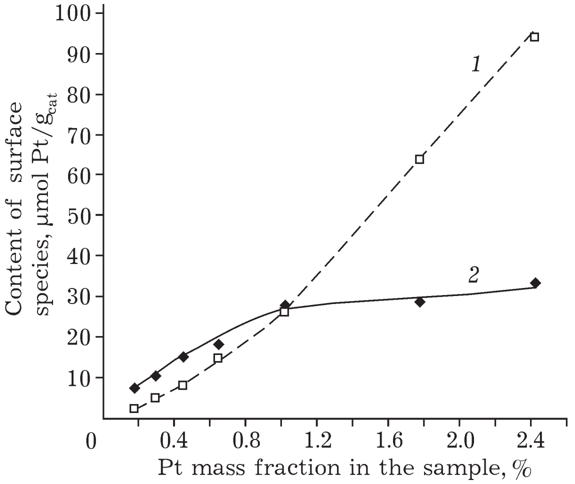

Fig. 3. Distribution of platinum involved in the desorbable (*1*) and non-desorbable (*2*) species for the samples with different metal content [25].

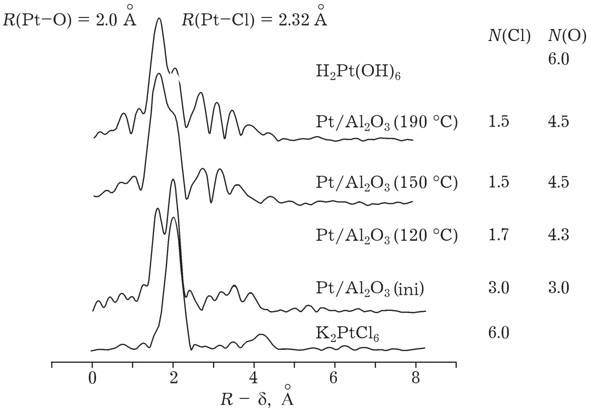

Fig. 4. Results of studying platinum (IV) chloride complexes adsorbed onto the surface of Al_2O_3 (C_{Pt} = 2 mass %) before and after hydrothermal treatment at 120, 150 and 190 °C, as well as standard compounds $K_2[PtCl_6]$, $H_2[Pt(OH)_6]$ by EXAFS method [16].

However, the EXAFS spectra of the adsorbed complexes (see Fig. 4) demonstrated increasing the reflexes of the second and third platinum coordination sphere with making the conditions of the hydrothermal treatment more severe. This fact may indicate that alongside with increasing the contribution of the coordination fixation of metal complexes, making their hydrolysis more profound causes a polycondensation process to be possible, which results in the formation of polynuclear structures with the coordination number with respect to oxygen close to 5. The theoretical possibility of forming Pt–O(OH)–Pt bond was demonstrated in the studies concerning model platinum (IV) hydroxo complexes under hydrothermal treatment conditions with the use of spectral and X-ray diffraction methods [35].

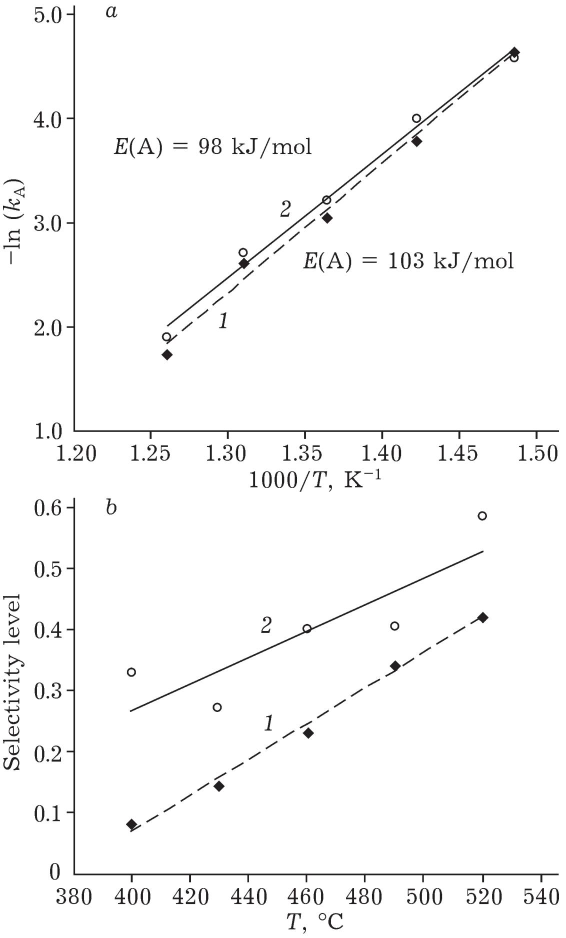

Fig. 5. Reaction constant (*a*) and reaction selectivity level (*b*) for the aromatization depending on the temperature of n-heptane dehydrocyclization (pretreatment conditions: T_{H_2} = 450 °C, 3 h; the reaction conditions: P = 10 atm, the mass flow rate of *n*-heptane 15 h^{-1}, the molar ratio H_2/C_7 = 5): *1* – initial sample 1.0 % Pt/Al_2O_3, *2* – after hydrothermal treatment (150 °C, 6 h).

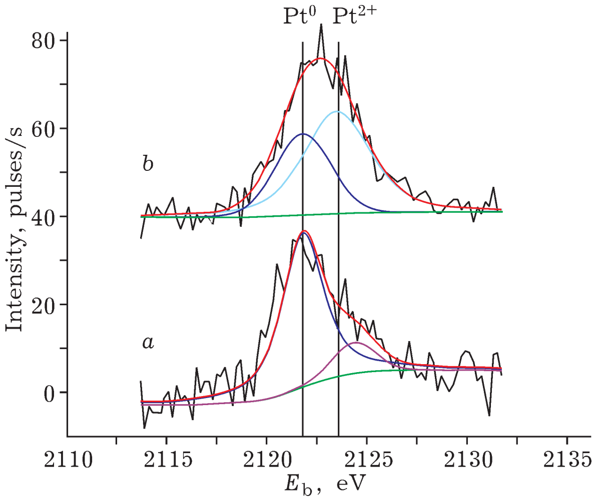

Fig. 6. XPS spectra of Pt/Al_2O_3 samples: initial (*a*) and after hydrothermal treatment (*b*). Mass fraction of platinum 1 %, T_{H_2} = 450 °C, 2 h, SPECS (Germany), monochromatic radiation AgL_α (H = 2984.3 eV) [38].

It was found that catalysts for hydrocarbon conversion obtained from the coordinationally fixed precursor exhibited a number of specific catalytic properties comparing to the traditional catalysts obtained *via* using a precursor less uniform in composition. There was a high selectivity concerning the dehydrocyclization of alkanes observed, as well as a higher activity in the dehydrogenation of cyclohexane, whereas the activity in the hydrogenation of benzene and hydrogenolysis of C–C bonds simultaneously decreased [14, 36]. As an example, Fig. 5 demonstrates the results of the comparative investigation of the catalysts in converting *n*-heptane within the temperature range of 400–520 °C. It is demonstrated that with the close aromatization activity (see Fig. 5, *a*) the selectivity with respect to the mentioned target reaction (curve *b*) is much higher for the sample prepared with the use of hydrolyzed platinum complexes as a precursor.

The reason for the differences in the adsorption and catalytic properties of the catalysts obtained from the coordinationally fixed precursor could consist in different electronic states of the applied platinum (at close dispersity level values) [37].

We compared the $Pt3d_{5/2}$ levels in the X-ray photoelectron spectra for the emission of

AgL_α samples obtained according the traditional scheme and with the use of the thermal hydrolysis stage [38]. The sample obtained with the hydrolyzed precursor (T = 120 °C, 3 h) demonstrated a shift of the platinum line towards higher energy values (Fig. 6). The decomposition of the XPS spectra allowed us to distinguish both platinum, whose valence state is close to that of metal Pt^0 (E_b = 2121.8 eV) and a charged form of the metal (E_b = 2123.5 and 2124.4 eV) for 1 % Pt/Al_2O_3 samples reduced in hydrogen at 450 °C [39]. It should be noted that the sample obtained from the hydrolyzed coordinationally bound precursor, demonstrates the percentage of platinum in the oxidized state, close to Pt^{2+}, to be higher to a considerable extent comparing to the samples prepared with no thermal hydrolysis stage. This effect seems to result from a partial conservation the bond between platinum and the surface groups of the carrier.

SURFACE TRANSFORMATIONS OF ADSORBED COMPLEXES AT THE DRYING STAGE

The analysis of publications for recent decades demonstrated that in a multi-stage chain of preparing supported catalysts, in particular concerning the system of Pt/Al_2O_3, a mandatory catalyst drying stage within the temperature range of 25–200 °C is generally considered only a procedure for removing the solvent from the pores of the carrier, with no taking into account any possible chemical processes [40]. Thereby one unwittingly ignores the possibility of the molecular design of precursors at this stage, as well as the importance of the chemical composition, structure, bond nature of metal complexes with carriers before the stages of a high-temperature heat treatment for the formation of final catalyst properties. Only a number of studies [23, 24, 41] demonstrate that the mentioned stage results in further transforming the platinum complexes adsorbed on the oxide surface. However, the processes observed are described on a qualitative level, whereas particular chemical reactions are only postulated.

The authors of [38] focused their main attention on the analysis of the transformation of platinum complexes adsorbed on the oxide surface in the course of drying at 25 and 120 °C, as well as revealing the role of chemical processes occurring at these stages in the formation of the properties of catalyst metal centres. The samples synthesized those represent platinum (IV) complexes chemisorbed onto the surface of γ-Al_2O_3 being different in the drying time, were investigated by means of electron spectroscopy (ESDO), ^{195}Pt NMR, gradient elution and TPR methods. It was found that with the increase in the drying time from 1 to 50 h an increase in the hydrolysis level of chloroplatinate was observed, simultaneously an increase in the percentage of non-desorbable platinum species was registered (from 10 to 60 %). To all appearance, the removal of moisture initiates the transition from outer-sphere complexes retained by electrostatic forces

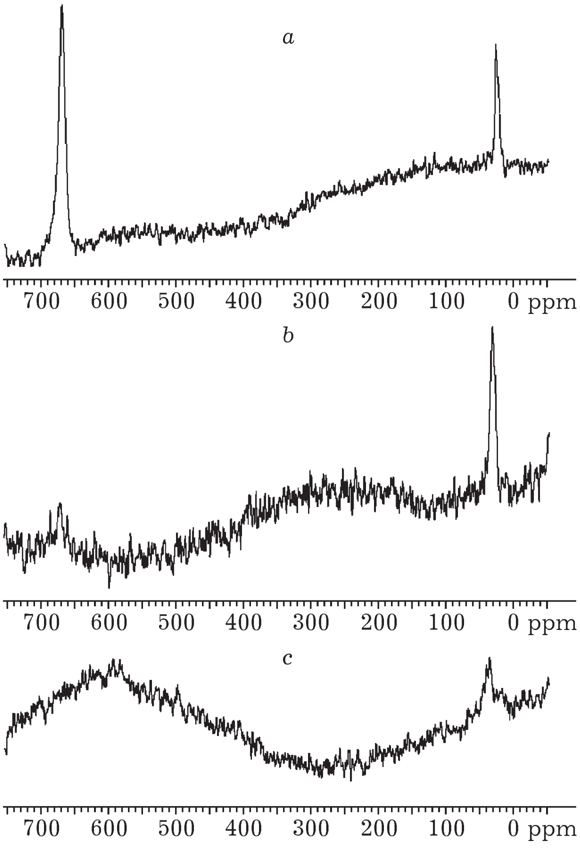

Fig. 7. NMR spectra of ^{195}Pt MAS platinum complexes adsorbed on γ-Al_2O_3 (C_{Pt} = 4.5 mass %; Bruker Avance III 400 MHz NMR spectrometer with multicore sensor SB4; sample rotation frequency at magic angle 104 Hz; the standard $H_2[PtCl_6]$ [38]): *a* – fresh-dried sample, *b*, *c* – sample additionally dried during 2 and 6 h, respectively.

to inner-sphere complexes bound with the surface through the coordination bond.

This conclusion is supported by the results of studying the adsorbed complexes by means of ^{195}Pt MAS NMR [38]. From the analysis of the NMR spectra it follows that an as-dried sample (Fig. 7, *a*) exhibits a weak electrostatic platinum (IV) interaction with the surface of the carrier with no considerable distortion of their geometry [19]. In this case the adsorbed platinum species are presented by chloride complexes $[PtCl_6]^{2-}$ (10 ppm) and monosubstituted chloro-hydroxo complexes $[PtCl_5(OH)]^{2-}$ (660 ppm). Further drying the sample under natural light (see Fig. 7, *b*) promotes a significant reduction in the intensity of the second signal, which confirms the ability of the hydrolyzed species of platinum to exhibit a more strong coordination interaction. A longer drying process is accompanied by a significant hydrolysis of the adsorbed complexes, which results in an increase in the proportion of coordinationally bound complexes and, as a consequence, in an almost complete disappearing of the NMR signals (see Fig. 7, *c*).

The effect of the chemical composition of the adsorbed complex, and especially that of the nature of its bonding with the surface was clearly demonstrated in the TPR of the samples. In the case of an “as-dried” sample, the TPR profile demonstrated (Fig. 8) a significant fraction of hydrogen (about 50 %) to be absorbed at low temperature values with the maximum absorption rate at 80 °C. When the ratio of platinum forms was close to equilibrium (drying time 50 h), a low-temperature peak of hydrogen absorption decreased to a considerable extent, whereas the main region of hydrogen absorption was in correspondence to the temperature range of 150–300 °C. The reduction conditions are determined by the nature of bonding, by the strength of interaction between the metal complexes and the carrier to determine the dispersity level of platinum particles formed (Table 1). The dispersity level of platinum deposited in these samples after reduction in hydrogen at 450 °C was measured using a technique of hydrogen and carbon (II) oxide pulse chemisorption. The presence of readily desorbed complexes fixed according to the ion-exchange mechanism, caused the formation of larger particles, whereas the measures directed on enhancing the interaction between the metal surface groups and the carrier, promote increasing the dispersity level of supported metal particles despite the increase in the reduction temperature. In this case, the possibility of obtaining fine platinum is realized, bypassing the stage of a high-temperature (120, 400 °C) oxidation treatment (see Table 1).

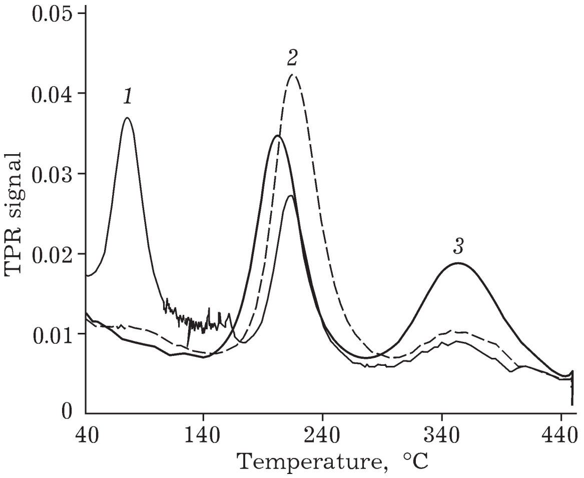

Fig. 8. TPR profiles for the adsorbed platinum complexes, different in time and drying temperature (C_{Pt} = 0.3 mass %): *1* – 25 °C, 1 h; *2* – 25 °C, 50 h; *3* – 120 °C, 1 h.

TABLE 1

Results of chemisorption measurements for the samples (C_{Pt} = 0.3 mass %)

Treatment conditions	TPR		*D*, %	
	μmol/g	ΣH_2 /Me	H_2	CO
Drying at 25 °C, 1 h	35.1	2.3	34	25
Drying at 25 °C, 50 h	42.3	2.8	85	68
Drying at 120 °C, 6 h	50.5	2.8	86	56
Calcination at 400 °C, 3 h	31.5	1.8	85	67

Note. Determination of the dispersion level (*D*) was carried out after the reduction of samples in hydrogen at 450 °C.

According to ESDO, increasing the processing temperature up to 120 °C for samples preliminary dried at 25 °C during 50 h did not result in changing the chemical composition of the platinum complexes [38]. However, under the TPR conditions, the increase in the drying temperature resulted in a considerable increase in the absorption of hydrogen within the region of 350 °C (see Fig. 8). In this case, the increase in the percentage of difficult-to-reduce platinum species could be connected with increasing the probability of multi-centred coordination fixing the precursor resulted from the activation of additional, less basic OH groups on the surface of aluminium oxide. In addition, at high temperature values there could be a condensation of hydrolyzed platinum species to form polynuclear hydroxo complexes those are also characterized by a high temperature of reduction [35].

CONCLUSIONS

In this paper, we performed the analysis of studies aimed at revealing the patterns of the active component formation. The main attention was paid to the transformation of a metal complex precursor at the initial stages of the synthesis.

So, the level of changing the ligand environment of platinum can be adjusted in a homogeneous medium via the action of light, temperature, as well as via the introduction of Pd(II) complex as a catalytic additive to obtain thus a preset composition of the precursor before its adsorption. In order to study the interaction between an adsorbed metal complexes and a carrier, it is convenient to use simple desorption techniques those allow quantitatively differentiating the adsorbed species depending on the nature of their binding with the surface either with the use of the competitive adsorption of specially chosen anions, or by varying the pH value of the oxide surface.

The investigation of the composition and the amount of metal complexes in the solutions of eluates as well as on the surface of aluminium oxide before and after the desorption revealed at least three species of existing precursors those differ in the composition of metal coordination sphere and in the bond strength with respect to the carrier: 1) readily desorbed ion-exchange species with the general formula $[PtCl_5(OH)]^{2-}$ retained by the carrier due to electrostatic forces, 2) strongly bound desorbable species characterized by a greater level of hydrolysis, to all appearance, $[PtCl_4(OH)_2]^{2-}$, and 3) strongly bound non-desorbable hydrolyzed complexes with the general formula $[PtCl_2(OH)_4]^{2-}$ fast retained by the carrier at the expense of several coordination bonds. In this case, the main direction of metal complex transformation during the formation of the catalyst consists in increasing the level of their hydrolysis according to the Scheme from ion exchange complexes (reaction **1**) to the complexes fixed via the coordination bond (reaction **3**) through intermediate species. However, in itself the hydrolysis represents a necessary but not sufficient factor for understanding of the real scheme concerning the transformation of chloroplatinate. Of critical importance is the fact that the hydrolysis involves not only outer-sphere water molecules, but also the structural OH groups of aluminium oxide which in this case should be considered a reagent. As the result of this, the electrostatic interaction at the stages of impregnation and especially drying is replaced predominantly by coordination bonding with the OH groups of the carrier. The tendency of the precursors to the formation, to all appearance, of most thermodynamically favourable coordination structures represents a driving force of their transformation. The process is finished at the specific centers of the carrier, where the substitution level of inner-sphere ligand in the metal complexes by the OH groups of the carrier amounted up to 4 for the octahedral complexes of platinum.

In order to increase the content of the coordinationally fixed species of complexes, it is efficient to use thermal hydrolysis of the adsorbed chloride precursor (hydrothermal treatment) within the temperature range of 100-150 °C, which provides, to all appearance, not only accelerating the hydrolysis of chloride complexes, but also activating an additional amount of the OH groups of the carrier.

The catalysts for the conversion of hydrocarbons obtained from the coordinationally fixed platinum species are characterized by a high proportion of platinum ionic species and exhibit a number of specific catalytic properties such as a high selectivity with respect to the dehydrocyclization of alkanes, a greater activity with respect to the aromatization of paraffins and the dehydrogenation of cyclohexane, a simultaneous decrease in activity with respect to the hydrogenation of benzene and hydrogenolysis of C–C bond.

The established quantitative correlations between different precursor species at the early stages of catalyst preparation and the knowledge concerning the laws of the active component formation depending on the type of bonding the precursors with the carrier and on their chemical composition could be used for targeted forming the fundamental characteristics of an active surface such as the dispersion level, the metal state, the level of interaction with the carrier. Thus, the generalizations presented in this work represent another stage on the way from an empirical approach in the development of catalysts to the ideology of chemical design on the base of profound understanding the formation of systems obtained by the application of metal complexes.

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