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Interaction between Pt(IV) and Pd(II) Chloro Complexes in Solution and on the γ-Al_2O_3 Surface

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Abstract—The conversions of a mixture of platinum(IV) and palladium(II) chloro complexes in aqueous solution and on the γ-Al_2O_3 surface at 25–150°C are reported. Heat treatment can initiate interaction between the complexes, both dissolved and adsorbed. The hydrolysis of the chloroplatinate ion is accelerated by the palladium chloro complex, whose composition remains unchanged.

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Thermodynamic and kinetic aspects of ligand exchange reactions, including the hydrolysis of platinum and palladium chloro complexes, have been reported in many publications since the 1970s [1–14]. These publications consider, mainly at the qualitative level, various factors accelerating the hydrolysis of the complexes in solution and focus much attention on the effect of temperature. However, most of these studies were performed at temperatures not exceeding 100°C. There have been only a few publications dealing with higher temperatures. For example, the stoichiometry of Pt(IV) and Pd(II) chloro complexes in aqueous solutions was investigated between 100 and 300°C [15]. These experiments, which were performed in acid media in the presence of excess Cl^- ions, demonstrated that the dissociation of the chloroplatinate ion can yield a mixture of the platinum monomer species $PtCl_6^{2-}$, $PtCl_5^-$, and $PtCl_4^0$ and the proportion of the latter increases at 300°C. At the same time, the composition of the palladium complex is less sensitive to temperature. The coordination number of palladium varies between 2.14 and 2.83 owing to the formation of polynuclear species. The composition of $PdCl_r(H_2O)_{4-r}^{2-r}$ ($r = 0$–4) complexes in aqueous solution at various Pd : Cl ratios at 5–125°C was studies by UV spectroscopy [16]. It was demonstrated that the $PdCl_4^{2-}$ complex in the presence of HCl and $HClO_4$ is low-sensitive to temperature. However, at lower solution acidities and temperatures above 50°C, there is a decrease of the absorption bands, which indicates a decrease in the amount of palladium in the solution. It was observed that the amount and formation rate of insoluble palladium species depends on the material of the cell walls. The wall effect was the weakest with quartz cells and was significant with titanium cells. Knowledge of platinum and palladium conversion pathways above 100°C is quite essential for understanding the chemical processes that take place in the synthesis of supported catalysts, when the metal complex solution is in the pore space of the support and heating is required for removing the solvent from the pores, particularly mesopores and micropores.

On the other hand, the wide use of bimetallic catalytic systems stimulates studies of the interaction between compounds of different metals at various synthesis stages, from preparation of the impregnating solution to high-temperature treatment of the supported complexes. In particular, this is true for the Pt–Pd/Al_2O_3 system, which has become especially interesting in the context of the problem of partially replacing platinum with palladium, a less expensive metal, in reforming catalysts [17]. However, there is only fragmentary information concerning the interaction between complexes of these metals in catalyst synthesis [18–25].

Here, we report the heat-induced conversions of platinum(IV) and palladium(II) chloro complexes simultaneously present in aqueous solution and on the γ-alumina surface in a wide temperature range of 25–150°C.

EXPERIMENTAL

Aqueous solutions of platinum and palladium chloro complexes were prepared from $H_2[PtCl_6]$ and $H_2[PdCl_4]$, which are typical precursors in the synthesis of commercial supported catalysts. Chloroplatinic acid solutions were prepared from the crystal hydrate $H_2PtCl_6 \cdot 6H_2O$ (OAO Aurat, USSR Specifications TU 6-09-2026-87). Chloropalladic acid solutions were prepared by dissolving $PdCl_2$ (OAO Aurat, USSR Specifications TU 6-09-2025-84) in a stoichiometric amount of hydrochloric acid followed by diluting with water to the preset concentration.

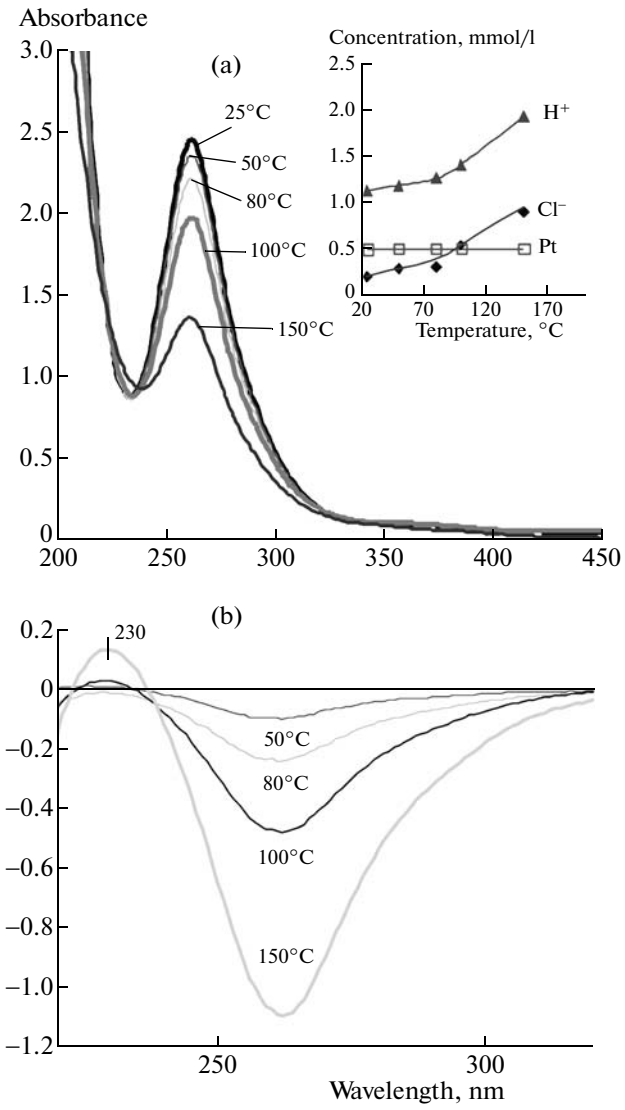

Fig. 1. Thermal hydrolysis of the H_2PtCl_6 solution (0.5×10^{-3} mol/l): (a) Temperature variation of the electronic absorption spectrum and of the Cl^-,H^+, and Pt concentrations in the solution; (b) difference spectrum relative to the spectrum of the unhydrolyzed platinum chloro complex.

The support was γ-Al_2O_3 (Condea) with a particle size of 0.1–0.2 mm, a specific surface area of 196 m^2/g, and a total pore volume of 0.55 cm^3/g. Texture parameters of the support were derived from nitrogen adsorption–desorption isotherms at 77.4 K using a Sorptomatic 1900 instrument. $H_2[PtCl_6]$, $H_2[PdCl_4]$, and their mixture were sorbed from excess amounts of aqueous solutions (5 g of Al_2O_3 : 50 ml of solution) at room temperature for 20 min to introduce 1 wt % of either metal. Next, the pellets were washed with water in order to remove the nonchemisorbed components of the solution from the pore space of the support.

The complexes dissolved in water and those supported on the alumina surface were heat-treated at 50, 80, 100, and 150°C for 30 min in the dark in titanium autoclaves with a glass insert. Solid samples air-dried at room temperature were placed into an autoclave, and water was added there so that the solid-to-liquid ratio was 1 : 10.

The platinum concentration in solutions was determined spectrophotometrically [26]; the palladium concentration, by atomic absorption spectroscopy [27] on an AA6300 Shimadzu spectrometer. The H^+ and Cl^- concentrations in solutions were determined with a SevenMulti ion meter (Mettler Toledo).

The UV spectra of metal complex solutions and those of powders of supported systems were recorded on a UV-2501 PC spectrophotometer (Shimadzu) with an ISR-240A diffuse reflectance attachment. For correct addition and subtraction, the spectra are presented in units of absorbance.

Hydrogen uptake and release were studied using an AutoChem II 2920 precision chemisorption analyzer (Micromeritics) with a thermal-conductivity detector. In temperature-programmed reduction (TPR) experiments, we used an H_2 (10%) + Ar mixture. Argon, hydrogen, helium, and oxygen were 99.999 vol % pure.

RESULTS AND DISCUSSION

Speciation of the Complexes in Aqueous Solution

The platinum chloro complex $[PtCl_6]^{2-}$ [28, 29] does not undergo any noticeable hydrolysis during solution preparation. Potentiometric measurements in a 0.5×10^{-3} M solution demonstrated that the amount of uncoordinated Cl^- ions does not exceed 5% of the total amount of Cl^- in the complex and remains practically invariable over 1 day. The H^+ concentration in the solution indicates the complete dissociation of H_2PtCl_6 [30].

Our experiments demonstrated that heat treatment speeds up the hydrolysis markedly, particularly above 80°C. This shows itself as an increase in the proton and uncoordinated chloride ion concentrations in the solution (Fig. 1a) and as significant changes in the electronic absorption spectrum of the complex. The decrease of the characteristic absorption band at 262 nm ($Cl^- \rightarrow Pt$ charge transfer) [26, 27] takes place against the background of an increasing absorbance around 230 nm. This can be seen more clearly in the difference spectrum (Fig. 1b) relative to the spectrum of the unhydrolyzed platinum chloro complex. Absorption at 230 and 270 nm characterizes the formation of the $[PtCl_4(OH)_2]^{2-}$ complex [28]. The spectroscopic data were confirmed by potentiometric data, which demonstrated that the hydrolysis of the chloroplatinate ion at 150°C proceeds, on the average, up to the second stage:

$$[PtCl_6]^{2-} + 2H_2O \rightleftarrows [PtCl_4(H_2O)_2]^0$$
$$\rightleftarrows [PtCl_4(OH)_2]^{2-} + 2Cl^- + 2H^+.$$

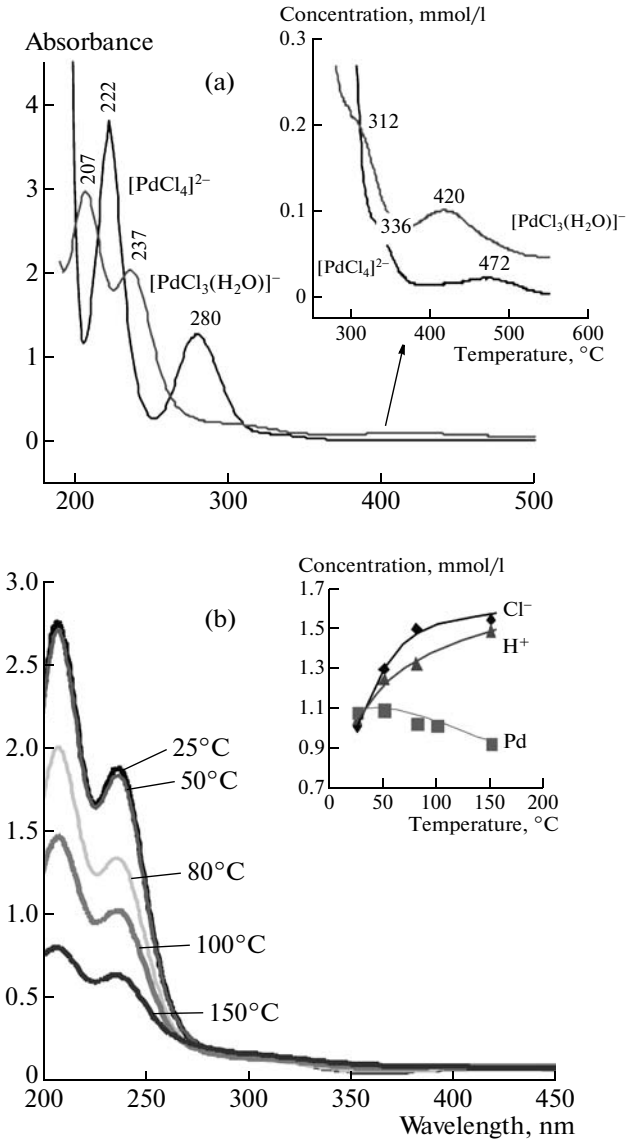

Fig. 2. Changes in the electronic absorption spectrum of the Pd(II) chloro complex caused (a) by the dissolution of the complex in water (for obtaining the spectrum of $[PdCl_4]^{2-}$, the complex was stabilized by introducing an extra amount of Cl^-) and (b) by thermal hydrolysis (H_2PdCl_4 concentration of 1.0×10^{-3} mol/l). Inset: Cl^-, H^+, and Pd concentrations in the solution as a function of the hydrolysis temperature.

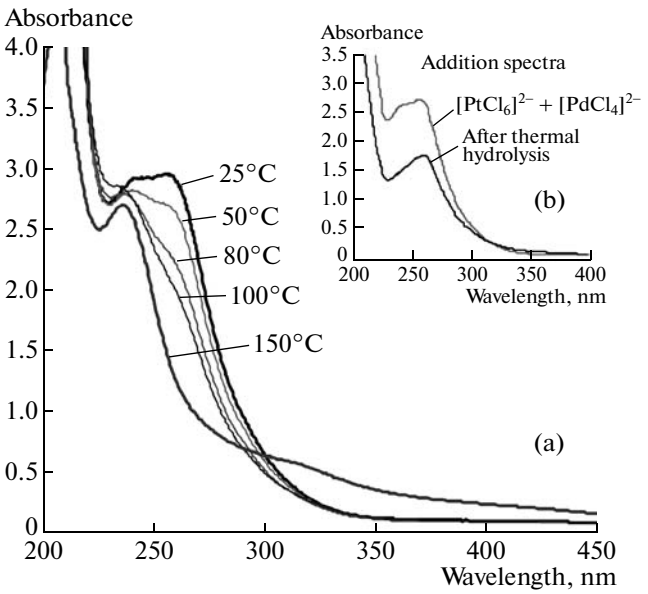

Fig. 3. Thermal hydrolysis of aqueous solutions of a mixture of H_2PtCl_6 and H_2PdCl_4: (a) experimental spectra of solutions held at 25 to 150°C; (b) addition spectra as the superposition of the spectra of the initial platinum and palladium complexes at $T = 25$°C and of the platinum and palladium complexes subjected to thermal hydrolysis at 150°C (Figs. 1a, 2b).

The palladium(II) chloro complex $[PdCl_4]^{2-}$ hydrolyzes to $[Pd(H_2O)Cl_3]^-$ during the preparation of its aqueous solution [28], as is indicated by the changes in the electronic absorption spectrum of the complex (Fig. 2). Heat treatment causes a further increase in the extent of hydrolysis up to the formation of the insoluble hydrolyzed species. The decrease of the absorption bands in the electronic spectrum (Fig. 2b) is due to the decrease in the palladium concentration in the solution (hydroxo complex precipitation) and is accompanied by an increase in the H^+ and Cl^- concentrations.

The heat-induced changes in the composition of the palladium complex can formally be represented as follows:

$$[PdCl_4]^{2-} + H_2O \rightleftharpoons [PdCl_3(H_2O)]^-$$

$$+ Cl^- \overset{T,\,H_2O}{\rightleftharpoons} Pd(OH)_2\downarrow + 4Cl^- + 2H^+.$$

Potentiometric data indicate that, as a result of hydrolysis at 150°C for 30 min, the molar ratio of palladium hydroxide to the aqua complex $[PdCl_3(H_2O)]^-$ is 1 : 4.

However, when the platinum and palladium complexes are simultaneously present in the solution, they show a different thermal behavior.

Figure 3 shows the electronic spectra of mixed solutions of the Pt(IV) and Pd(II) chloro complexes (1 : 2 mol/mol): (a) observed spectra and (b) addition spectra obtained under the assumption that there is no interaction between these complexes. Clearly, at $T =$ 25°C, the band shapes and intensities in the experimental spectra and those in the calculated spectra obtained by superposition of the spectra of the starting platinum and palladium complexes coincide. However, after the heat treatment of the initial solutions, the calculated and observed spectra are markedly different. When both metals are present simultaneously, the hydrolysis of the labile palladium complex is slower (the intensity of the characteristic charge trans-

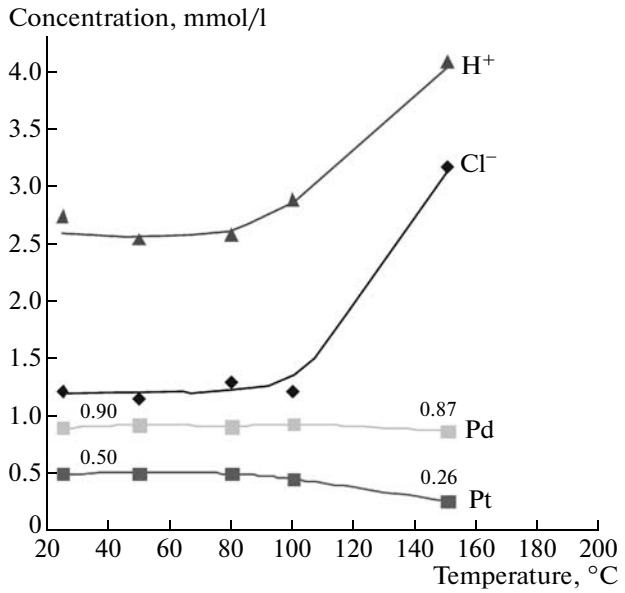

Fig. 4. Temperature dependences of the platinum, palladium, Cl^-, and H^+ concentrations in the solution of $H_2PtCl_6 + H_2PdCl_4$.

fer band at 237 nm is almost invariable). At the same time, the chloroplatinate ion undergoes deep hydrolysis (up to the formation of the insoluble hydroxo complex), whose rate under normal conditions is lower than the hydrolysis rate of $[PdCl_4]^{2-}$ by a factor greater than 10^6 [28]. The electronic absorption spectrum indicates a decrease of the chloroplatinate band (charge transfer band at 262 nm), and the platinum concentration in the solution decreases, while the palladium concentration remains nearly constant (Fig. 4). The formation of the hydrolyzed (aquated) species $[PtCl_5H_2O]^-$ from inert platinum(IV) chloro complexes in the presence of $[PdCl_4]^{2-}$ was also observed in simultaneous electrophoretic and spectroscopic studies of aqueous solutions of the complexes [31]. This effect takes place only when the solution contains an insufficient amount of HCl and is left standing for 1 h.

An analysis of the temperature-dependent component concentrations in the initial solution (Fig. 4) demonstrates that, in the aqueous solution containing $H_2[PdCl_4]$ and $H_2[PtCl_6]$ at $T = 25°C$, the H^+ concentration is governed by the dissociation of the acids and the Cl^- concentration is determined by the extent of hydrolysis of the palladium chloro complexes. The Cl^- concentration measured in the initial solution suggests that the hydrolysis (aquation) of $[PdCl_4]^{2-}$ under the given condition proceeds up to the first and, partially, second stages and the average composition of the complex is $[PdCl_{2.7}(H_2O)_{1.3}]^{0.7-}$. As the temperature is raised to 100°C, the hydrolysis of the platinum chloro complex, which shows itself as changes in the electronic spectrum, is not accompanied by a buildup of H^+ and uncoordinated chloride ions (Fig. 4). It is likely that heating accelerates ligand exchange in the complexes, which makes possible the migration of chloride ligands from the platinum(IV) complex to the palladium(II) complex with the formation of a platinum(IV) aqua complex. This process will be possible if the aquation of the platinum(IV) chloro complex is thermodynamically more favorable than the further aquation of $[PdCl_3(H_2O)]$:

$$[PtCl_6]^{2-} + H_2O \rightleftarrows [PtCl_5(H_2O)]^- + Cl^-,$$
$$\log K_6(\text{st}) = 2.20\,[32];$$

$$[PdCl_3(H_2O)]^- + H_2O \rightleftarrows [PdCl_2(H_2O)_2] + Cl^-,$$
$$\log K_3(\text{st}) = 2.68\,[33],$$

where K_3 and K_6 are the cumulative stability constants of the palladium and platinum complexes, respectively. Therefore, the capacity of the $[PdCl_2(H_2O)_2]$ complex for binding Cl^- ions to form $[PdCl_3(H_2O)]^-$ is stronger than the capacity of $[PtCl_5(H_2O)]^-$ for binding these ions into $[PtCl_6]^{2-}$. The literature contains only limited information concerning the cumulative and stepwise stability constants of these complexes, particularly for the kinetically inert Pt(IV) complexes. However, it was reported [32, 33] that the equilibrium constant of reaction (I) ($[PtCl_6]^{2-}$ aquation) is indeed 3 times larger than that of reaction (II).

Heat treatment at a higher temperature of 150°C causes the inner-sphere deprotonation of the aqua ligands of the platinum complex, yielding the insoluble platinum hydroxo complex. This is accompanied by a stoichiometric increase in the H^+ concentration in the solution from 2.6 to 4.0 mmol/l (Fig. 4).

The sharp increase in the concentration of uncoordinated chloride ions at 150°C is due to not only the hydrolysis of the platinum(IV) chloro complexes, but also the partial hydrolysis of the palladium(II) chloro complexes, as is indicated by the weakening of the absorption band at 237 nm in the electronic spectrum (Fig. 3). Note that palladium(II) stays in the form of a chloroaqua complex because the aqua ligands in its coordination sphere are less prone to deprotonation than the aqua ligands coordinated to platinum(IV). This is due to the fact that the lower oxidation state of the metal the lower the ionicity of the O–H bond in its aqua ligand. For example, the acid dissociation constant of water in the Pt(IV) aqua complex was reported to be two orders of magnitude larger than that of water in the similar complex of Pt(II) [34].

There have been reports concerning a similar accelerating effect of a Pt(II) complex on the hydrolysis of Pt(IV) chloro complexes [13, 28]. The authors of these report believe that this process takes place via the formation of the pentacoordinated platinum complex $[PtCl_5]^{3-}$ and a dinuclear intermediate containing Pt(II) and Pt(IV).

Speciation of the Complexes Adsorbed on the Al_2O_3 Surface

The chemical composition of the surface platinum(IV) and palladium(II) complexes adsorbed on the alumina surface was characterized by diffuse reflectance spectroscopy. Figure 5a presents the spectra of the platinum and palladium chloro complexes adsorbed on the γ-Al_2O_3 surface. The spectrum of the chloroplatinate shows two absorption bands at 36700 and 43100 cm^{-1} ($1t_{2u} \rightarrow 2e_g$ transition), which are due to $Cl^- \rightarrow Pt$ charge transfer, and two weak ones at 28500 and 21700 cm^{-1}, which are due to *d–d* transitions ($2t_{1u}, 2t_{2g} \rightarrow 2e_g$). According to the literature [28–30], the alumina surface in this case contains both $[PtCl_6]^{2-}$ ions and the partially hydrolyzed species $[Pt(OH)_xCl_y]^{2-}$. After hydrothermal treatment, the diffuse reflectance spectrum (Fig. 5b) shows a substantially lower absorption intensity around 36700^{-1} and the absorption maxima are shifted to higher frequencies. This is due to the appearance of oxygen ions in the coordination sphere, which means a deeper hydrolysis of the adsorbed species [35, 36].

The initial spectrum of the supported palladium complex (Fig. 5a) does not clearly show the absorption bands characteristic of the complex ion $[PdCl_4]^{2-}$. Only metal–ligand charge transfer bands at 43800 cm^{-1} ($2e_u \rightarrow 3b_{1g}$ transition) and 34800 cm^{-1} ($3e_u, b_{2u} \rightarrow 3b_{1g}$) are assignable to this complex [7]. At the same time, the appearance of absorption around 23300 cm^{-1}, which is due to *d–d* transitions ($2e_g \rightarrow 3b_{1g}$), indicates the presence of hydrolyzed palladium species, whose likely composition is $[PdCl_3(H_2O)]^-$ [26, 27, 34]. Hydrolyzed palladium species, even if more aquated ($[PdCl_2(H_2O)_2]^0$), were also identified in an earlier study of the adsorption of palladium chloro complexes on alumina in a wide metal concentration range [37].

Heat treatment reduces the absorbance at high frequencies (Fig. 5b). This can be due to the increase in the number of aqua ligands in the coordination sphere of palladium [28]. In addition, there is marked broadening of the absorption band at 23300 cm^{-1}, which is likely caused by the formation of polynuclear species. It was indeed demonstrated earlier [38, 39] that the formation of the dinuclear complex $[Pd_2Cl_6]^{2-}$ shifts the absorption maximum in the visible region to shorter wavelengths, specifically 23200 cm^{-1}, and raises the intensity of this band. The capacity of palladium to form polynuclear complexes upon hydrolysis was studied in detail [40–43].

Without heating, the composition of a given surface complex is unaffected by the presence of the complex of the other metal, as is indicated by the qualitative similarity between the experimental spectrum and the spectrum obtained by adding the spectra of the individual complexes (Fig. 6a). After thermal hydrolysis, the spectrum of the adsorbed mixture of the Pt(IV) and Pd(II) chloro complexes is markedly different

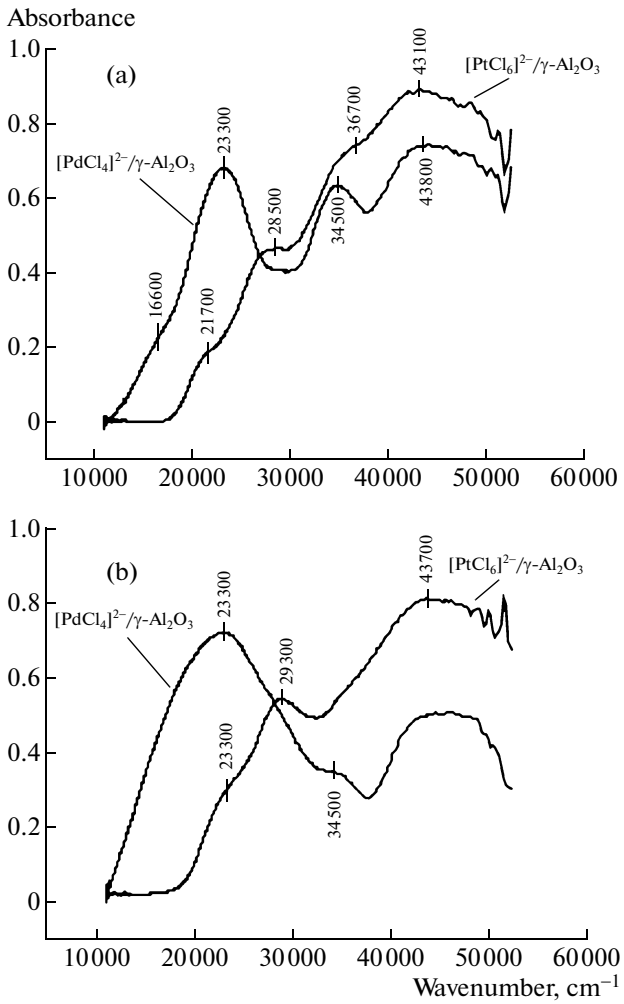

Fig. 5. Diffuse reflectance spectra of the Pt(IV) and Pd(II) chloro complexes on the γ-Al_2O_3 surface (a) before and (b) after hydrothermal treatment. The metal contents of the samples is 1 wt %. The hydrothermal treatment temperature is 120°C.

from the addition spectrum of the individual complexes hydrolyzed under the same conditions (Fig. 6b): the former exhibits no increase in absorption intensity at ~23000 cm^{-1} characteristic of hydrolyzed palladium species (Fig. 5b). At the same time, the absorption band at 34500 cm^{-1} has the same intensity as the band of the initial, unhydrolyzed palladium complex. An analysis of the spectra presented in Fig. 5 suggests that the absorption band at 29700 cm^{-1} should be assigned to platinum complexes, and the shift of this band to higher frequencies relative to its positions in the spectra of the initial and hydrolyzed complexes is evidence that the platinum complex in the presence of palladium undergoes deeper hydrolysis.

Thus, the Pt(IV) and Pd(II) complexes adsorbed on the Al_2O_3 surface can interact under hydrothermal conditions, as in the case of their aqueous solutions. This interaction accelerates the hydrolysis of the chlo-

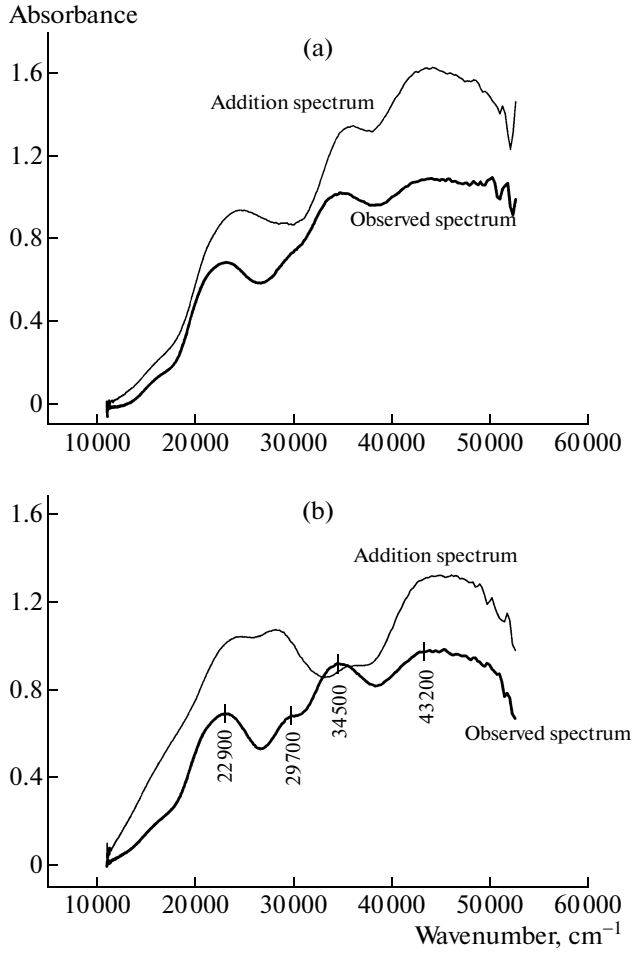

Fig. 6. Diffuse reflectance spectra of the Pt(IV) and Pd(II) chloro complexes coadsorbed on γ-Al_2O_3 (a) before and (b) after hydrothermal treatment.

roplatinate ion without changing the palladium chloro complex.

This result is in good agreement with TPR data.

Figure 7 presents the TPR profiles for the platinum and palladium chloro complexes separately chemisorbed on γ-Al_2O_3. The reduction of palladium give rise to two hydrogen uptake regions with uptake peaks at 60°C and above 300°C. In addition, the TPR spectrum shows a diffuse hydrogen evolution feature in the 150–250°C range, which is attributed [44] to the release of hydrogen adsorbed on the surface of reduced palladium particles. Platinum reduction takes place between 150 and 400°C, giving rise to a well-defined hydrogen uptake peak at 200°C and a shoulder at 330°C. These data are in good agreement with TPR data for the Pd/Al_2O_3 and Pt/Al_2O_3 systems [44, 45].

The TPR spectrum of the sample containing both of the adsorbed complexes is not the superposition of the TPR profiles of the monometallic samples. It shows a hydrogen uptake peak at 145°C along with the peaks due to the reduction of the platinum(IV) and

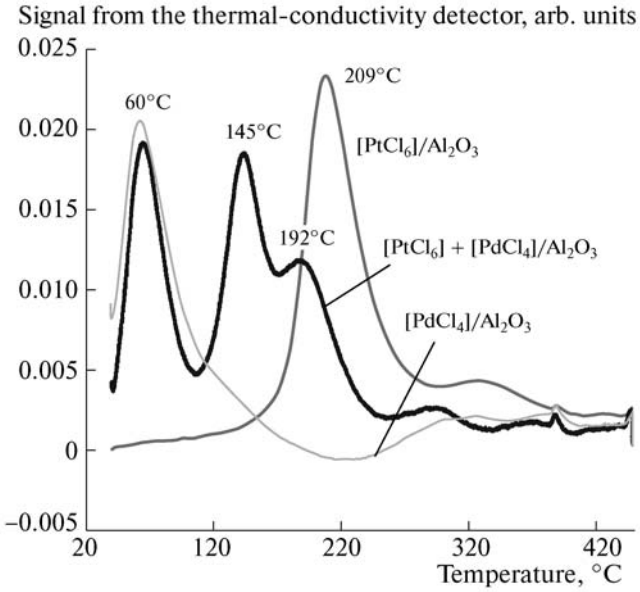

Fig. 7. TPR data for the Pt(IV) and Pd(II) chloro complexes adsorbed separately and together on γ-Al_2O_3.

palladium(II) chloro complexes. The appearance of this peak is attributed both to the formation of Pt-Pd bimetallic particles and to the reduction of part of the platinum complexes occurring at a lower temperature owing to hydrogen preactivation on palladium sites [18, 46, 47].

Hydrothermal treatment noticeably changes the TPR profiles of the platinum and, particularly, palladium complexes (Fig. 8a). In the case of platinum, it changes the intensity ratio between the low- and high-temperature peaks. As was demonstrated in earlier works [35, 36], the increase in the hydrogen uptake in the high-temperature region is due to the increase in the proportion of hydrolyzed, coordinatively bound platinum species.

In the case of palladium, the formation of Pd–O bonds via the hydrolysis of the chloride precursor facilitates the heterolytic breaking of the bond in the hydrogen molecule and the formation of palladium hydrides [18, 48]:

$$Pd_s\text{–}OH + H_2 \rightarrow Pd_sH + H_2O.$$

This reaction takes place below 25°C, and, in some studies [44, 45, 48, 49], the TPR technique was sufficiently sensitive to observe the corresponding hydrogen uptake peak in the 6–12°C range. Heating the sample to 70–100°C causes palladium hydride decomposition: $Pd_sH \rightarrow Pd_s + 0.5H_2$. This gives rise to a sharp hydrogen evolution peak in the TPR profile (Fig. 8a) [44, 46, 48, 49]. The appearance of the palladium hydride decomposition stage on passing from the surface palladium chloro complexes (N(O) = 1.2) to oxide species (N(O) = 3.8–4.3) was demonstrated in an earlier study [44].

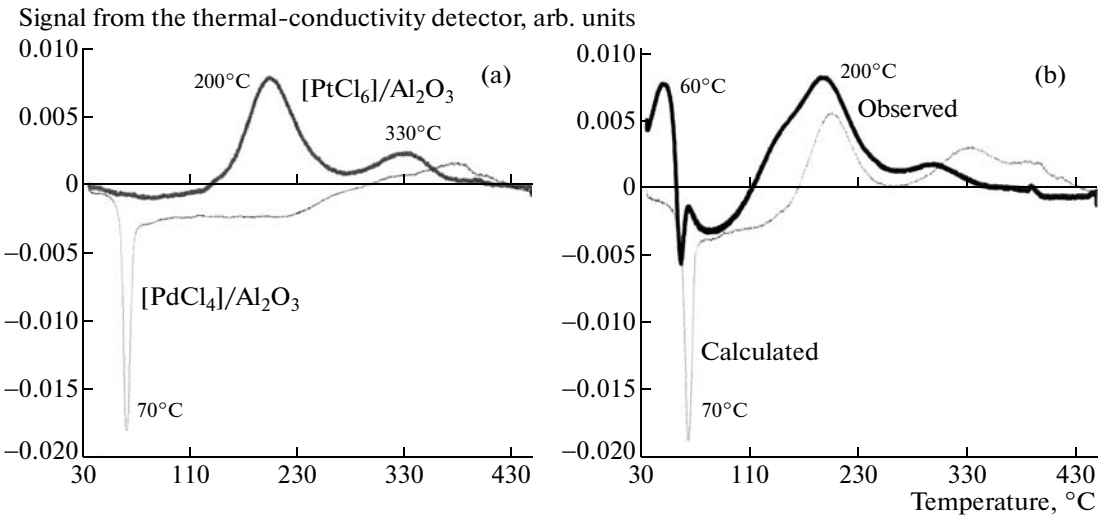

Fig. 8. TPR data for the thermally hydrolyzed Pt(IV) and Pd(II) chloro complexes supported on γ-Al_2O_3 (a) separately and (b) together. The dashed line in Fig. 8b is the superposition of the spectra shown in Fig. 8a.

The TPR spectrum of the adsorbed mixture of the platinum and palladium complexes after thermal hydrolysis is shown in Fig. 8b. For comparison, we present the profile obtained by superposition of the curves characterizing the reduction of the hydrolyzed monometallic samples (Fig. 8a). As distinct from the calculated curve, the observed profile indicates a decrease in the proportion of the hydrolyzed palladium species in the presence of the platinum(IV) complexes: firstly, there is a hydrogen uptake region with a peak at 60°C, which is due to the reduction of the palladium chloro complex; secondly, the magnitude of the "negative peak" is considerably lower.

CONCLUSIONS

Heat treatment of a mixture of platinum(IV) and palladium(II) chloro complexes in solution and those adsorbed on the alumina surface can initiate the interaction between these complexes. In this interaction, chloride ions are transferred from the tetravalent component to the divalent component.

This effect is essential for understanding the surface processes occurring during the synthesis of bimetallic supported catalysts. The introduction of Pt(IV) complexes can diminish the probability of the formation of large palladium(II) polyhydroxo complexes under hydrothermal conditions, which take place at the high-temperature stages of the synthesis and regeneration of supported catalysts, and thus can conserve the disperse state of palladium. On the other hand, palladium favors the reduction of platinum complexes at lower temperatures. This effect is significant for obtaining finer Pt or Pt–Pd particles.

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