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Effect of Surface Modification of γ -Al₂O₃ Using Oxalate Complexes of Aluminium on the Formation and Properties of Platinum Centres of Pt/Al₂O₃ Catalysts

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Abstract

Modification of the oxide surface of aluminium oxide with oxalate complexes of aluminium was carried out, followed by thermal treatment for the purpose of varying the ratio between the functional groups on the surface (OH groups, Lewis acid centres). It was established that the modification of γ -Al₂O₃ causes a 1.5-fold increase in the amount of adsorbed platinum (IV) complexes and the fraction of these complexes strongly bound with the surface of the support. The effect of γ -Al₂O₃ surface modification on the catalytic properties of the system Pt/Al₂O₃ was demonstrated. It was shown that an increase in the fraction of platinum forms strongly bound with the support causes an increase in the content of methylcyclopentane in the products of *n*-hexane isomerization and an increase in the selectivity of the formation of propylene in propane transformations.

Key words: γ -aluminium oxide, surface modification, chloride complexes of platinum, aluminium-platinum catalysts, adsorption mechanism

INTRODUCTION

Supported platinum catalysts of the Pt/ γ -Al₂O₃ family find broad application in various branches of industry. The most important directions of their use include large-scale processes, such as catalytic reforming of petrol and isomerization of normal alkanes C₅–C₆ [1, 2]. The preparation of Pt/ γ -Al₂O₃ catalytic systems includes the stages of the deposition of active metal, most frequently from the aqueous solution of H₂[PtCl₆], drying and thermal activation. Fixation of the molecular precursor of deposited metal on the surface of the support plays important part in the formation of catalytically active centres [1, 3–7]. At this stage, regulation of the strength of the interaction

between the metal complex and the support allows obtaining metal centres with necessary adsorption and catalytic properties. Two approaches are traditionally used for this regulation: one of them involves variation of the chemical composition of precursor, and the other one involves chemical modification of the support [1, 2, 8–10]. Thus, additional introduction of halogen promotes the uniform distribution of platinum over the grains of the support, allows one to enhance its acidity and stabilize a part of deposited platinum in the electron-deficient state [9, 10]. The introduction of the second or the third metal (Re, Sn) acting not only as diluents but also as modifiers of the electronic state of the active component has become widespread in the production of alu-

minoplatinum catalysts [2, 8, 10]. It is necessary to stress that the introduction of modifiers or promoters not only brings complications into the synthesis of the catalyst but also may lead to non-reproducibility of the properties of the resulting multicomponent system.

It is known that the character of the interaction between metal complex and the support is determined by the chemical composition of the precursor and the nature of adsorption centres on the surface of the support [1, 5–7]. It is accepted that these centres on the surface of the support are either hydroxyl groups [1, 3–7] or coordination-unsaturated aluminium cations (Lewis centres) [11, 12]. It is yet unknown to what extent it is possible to achieve the optimal strength of the interaction between the precursor and the support. Thus providing the necessary adsorption and catalytic properties of supported metal within the same catalytic composition due to changes in the ratio of functional groups on the surface of the support without introducing chemical additives (modifiers or promoters).

Previously we proposed an approach allowing one to vary the relative content of surface groups with different nature in γ aluminium oxide with the surface of the same chemical composition [13]. The essence of the proposed operation was chemisorptive fixation of the oxalate complexes of aluminium (3 mass % calculated for Al_2O_3) on the surface of initial aluminium oxide. Subsequent thermal decomposition of adsorption complexes in the oxidative atmosphere leads to the formation of supported oxide compounds of aluminium. For identical qualitative chemical composition, structural and texture characteristics, the obtained system 3 % $\text{Al}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ differed from initial $\gamma\text{-Al}_2\text{O}_3$ in the ratio of functional groups on the surface. The difference was in the smaller (in comparison with $\gamma\text{-Al}_2\text{O}_3$) fraction of OH groups bound with pentacoordinated aluminium atoms, and in the smaller concentration of weak Lewis acid centres.

The goal of the present work was to study the effect of changes in the composition of the functional coating of the support surface caused by modification using the above-described procedure, on the nature of interaction between the precursor and the support and on the properties of the formed platinum centres of Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalysts.

EXPERIMENTAL

Sample preparation

We used $\gamma\text{-Al}_2\text{O}_3$ (Condea) with grain size 0.1–0.25 mm, specific surface determined by BET $S_{\text{BET}} = 202 \text{ m}^2/\text{g}$, adsorption pore volume $0.55 \text{ cm}^3/\text{g}$, and effective pore diameter 11.1 nm. The concentrations of sodium and iron were 0.003 and 0.21 mass %, respectively. Modification of $\gamma\text{-Al}_2\text{O}_3$ using the oxalate complexes of aluminium was carried out according to the procedure described in [13]. Impregnating solutions of aluminium oxalate were prepared from crystal hydrate $\text{Al}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ of “ch.” reagent grade (Reakhim). Aluminium oxide samples for subsequent examination were prepared with the modifier in the concentration corresponding to the maximal amount of complexes fixed by chemisorption (3 mass % calculated for Al_2O_3). After drying at a temperature of 120°C , the samples were annealed at 550°C for 3 h to decompose adsorbed oxalate complexes and to form the oxide compounds of aluminium on the surface of $\gamma\text{-Al}_2\text{O}_3$.

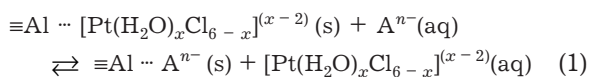
During the synthesis of supported minoplatinum catalysts, we used the aqueous solutions of chloroplatinic acid with the required concentrations as the precursor. To prepare these solutions, we used crystal hydrate $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$ of “ch.” reagent grade (Aurat Co., TU 6-09-2026–87). To record the isotherms of $\text{H}_2[\text{PtCl}_6]$ adsorption on aluminium oxide supports, we used the method of separate weighted portions with the ratio of support mass to the mass of $\text{H}_2[\text{PtCl}_6]$ solution equal to 1 : 25 ($(20 \pm 1)^\circ\text{C}$). Platinum concentration in solutions was determined by means of photometry. The method is based on the formation of coloured complex with tungsten chloride in hydrochloric solution [14].

The samples of supported platinum catalysts were prepared by impregnating the support in the excess amount of the solution. Platinum sorption was carried out for 20 min. In this case, almost complete extraction of platinum from solution is achieved, while the dissolution of the support and the release of Al^{3+} into solution may be neglected because of very low rate of this process [15]. After impregnation, the samples were thoroughly washed with

water to remove non-chemisorbed components of the solution from the pores of the support. If necessary, the air-dried samples of supported catalysts for afterwards subjected to thermal oxidative treatment at a temperature of 120 and 550 °C.

Methods of sample examination

Gradient elution (GE). To estimate the strength of the interaction between metal complex and the surface of the support, we used GE procedure [3, 4, 7, 16]. This method involves gradual desorption of fixed anionic complexes of platinum followed by the analysis of platinum concentration in the effluent. To form the eluent, we used the solutions of mono-, di- and trihydric acids: perchloric (5.0 g-equiv./L), oxalic (2.0 g-equiv./L) and citric (2.0 g-equiv./L). These acids do not destroy this support substantially during sorption; they do not interact with the chloride complexes of platinum and what is more, they differ in the selectivity of adsorption on aluminium oxide [17, 18]. The system supplying eluting solution provided a smooth increase in the desorbing strength of the eluent due to gradual increase in the concentrations of acids simultaneously entering the column with the sample. Gradual displacement of the platinum complexes of ion-exchange nature from the surface of the support into the solution by the competing acid anions A^{n-} was achieved, depending on the strength of the interaction of metal complexes with the oxide surface:



The sample under study, with the mass of 4.000 g, was placed into a glass column 10 mm in diameter and 400 mm high. Elution rate was 0.5–1.0 mL/min. Platinum concentration in the effluent was determined by means of photometry. The profile of GE was plotted on the basis of the results of analyses. This plot shows the dependence of Pt concentration in desorbed complexes on the volume of eluent that passed through the sample.

Platinum content of the catalysts after GE was determined photometrically. The method involves dissolution of a weighted portion of

preliminarily dried and annealed sample in 50 % sulphuric acid, followed by boiling of the resulting solution in the presence of H₂O₂ and HCl. Further photometric determination of platinum was carried out using the method based on the formation of a coloured complex with tin chloride in hydrochloric solution [14].

Thermoprogrammable reduction (TPR). Chemisorption of H₂ and CO. Investigation of the processes of hydrogen absorption–evolution was carried out using the precise chemisorption analyser AutoChem II 2920 (Micrometrics) with the thermal conduction detector. The samples were dried preliminarily at room temperature. In the experiments on TPR we used a mixture of 10 % H₂–Ar. The purity of gases used in the experiments was 99.999 vol. %. Reduction was performed within temperature range 35–500 °C with heating rate 10 °C/min.

For the quantitative analysis of TPR results, the obtained profiles were subjected to deconvolution using Pearson's function IV; the possibility to use this function for the expansion of asymmetric TPR profiles was demonstrated in [19]. We used the following form of this function:

$$I = I_0 \left(1 + \frac{x^2}{\Delta^2} \right)^{-m} \exp \left(-v \arctan \frac{x}{\Delta} \right) \quad (2)$$

$$x = 2(T - T_0) \sqrt{2^{1/m} - 1} \quad (3)$$

where I_0 is the intensity of peak maximum, V ; T_0 is the position of the maximum, °C; Δ is the peak half-width, °C; v and m are the parameters of peak shape characterising its asymmetry and excess, respectively. The convergence of experimental and calculated (superposition of the components) TPR curves was evaluated with the help of correlation coefficient which was not less than 0.984 in all cases.

Chemisorption of hydrogen or carbon oxide was carried out to determine the dispersity of deposited metal in catalyst samples reduced preliminarily. A mixture of 10 % H₂–Ar or 9 % CO–He was supplied in pulses after equal time intervals into the flow of inert carrier gas – argon or helium, respectively. Dosing was carried out at room temperature till the establishment of the constant signal of the detector. Calculation of metal dispersity was carried out taking into account sorption stoichiometry H/Pt = 1 : 1, CO/Pt = 1 : 1 [20–22].

Catalytic tests in propane dehydrogenation.

A model reaction to characterize the metal centres of Pt/Al₂O₃ catalysts was propane dehydrogenation. The reaction was carried out in a flow reactor with the immobile catalyst layer (weighted portion 1.0 g) at a temperature of 550 °C. The flow of the raw mixture was formed by mixing gaseous hydrogen and propane. The molar ratio H₂/C₃H₈ was 0.25, and the mass rate of raw mixture supply (calculated for propane) was 4.0 h⁻¹. Before the start of experiments, catalyst samples were activated in hydrogen flow at a temperature of 550 °C for 1 h. Product composition was analysed by means of gas-liquid chromatography in the online mode using a Khromos GK_h-1000 chromatograph equipped with Rt-Alumina Plot column (50 m × 0.53 mm) and flame ionisation detector. Chromatographic examination was carried out in the isothermal mode at the column temperature of 80 °C.

Catalytic tests in the transformations of *n*-hexane. Investigation of the catalytic properties of supported Pt/Al₂O₃ systems was carried out at atmospheric pressure using a microcatalytic setup in the pulsed regime. The reaction mixture was made by hydrogen saturation with hexane in a saturator at a temperature of 35.0 °C. During sample examination, a constant ratio of H₂/C₆H₁₄ = 2 was maintained; contact time was 5 s. Catalyst sample (a weighted portion of 0.5 g) was put in a U-shaped glass

reactor and activated before measurements in hydrogen flow at a temperature of 450 °C for 2 h. Tests were carried out within temperature range 250–450 °C. The pulse volume was 30 mL/mg of the catalyst. The initial reagent and the products of the reaction were analysed by means of gas-liquid chromatography in the online mode using a Carlo Erba Instruments chromatograph. The instrument was equipped with a flame ionisation detector and a capillary column (25 m × 0.2 mm) with immobile liquid phase SE-54. To improve chromatographic separation, analyses were carried out in temperature-programmable mode.

RESULTS AND DISCUSSION

Effect of the deposition of oxide compounds of aluminium onto γ -Al₂O₃ on the adsorption of chloride complexes of Pt(IV)

To study the effect of modification of γ -Al₂O₃ surface on the adsorption properties of the support with respect to chloride complexes of Pt(IV), the following adsorption isotherms were recorded (Fig. 1). They are satisfactorily described by Langmuir equation; their analysis by means of linear anamorphoses allowed us to calculate limiting adsorption and the constants of adsorption equilibrium.

It follows from the analyses of the data of adsorption experiments that the limiting adsorption resulting from the modification of the surface of γ -Al₂O₃ was 0.32 mmol Pt/g, which is 1.5 times higher than the corresponding value for initial aluminium oxide. The constant of adsorption equilibrium grows from 8.3 to 9.6 L/mol.

The observed increase in the adsorption capacity of γ -Al₂O₃ and the constant of adsorption equilibrium may be explained by changes in the composition of the functional coating of the surface as a result of modification. It was demonstrated in [13] that fixation of oxalate complexes is participated by 290 mmol/g of hydroxyl groups of initial aluminium oxide (at the ratio of complex/OH group = 1 : 1), while, according to the results of IR spectroscopy, the concentration of OH groups decreases by only 70 μ mol/g. The authors of [13] explained the obtained result by the formation of oxide compounds on the surface of γ -Al₂O₃; these com-

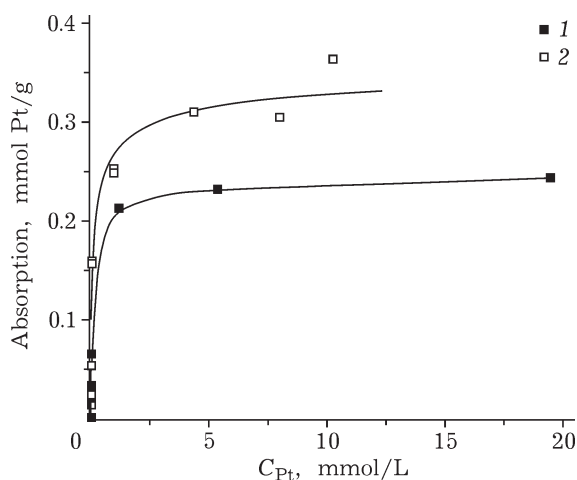


Fig. 1. Isotherms of H₂[PtCl₆] adsorption on the samples of aluminium oxide: 1 - γ -Al₂O₃, 2 - 3% Al₂O₃/ γ -Al₂O₃.

TABLE 1
Mass balance of desorption experiments

Supports	Pt content		Desorbed Pt, mass %
	in sample, mass %		
	before GE	after GE	
γ -Al ₂ O ₃	1.0	0.23	0.77
3% Al ₂ O ₃ / γ -Al ₂ O ₃	1.1	0.49	0.61

pounds possess their own hydroxyl coating which is likely to differ from the coating of the surface of initial support in the ratio of OH groups of different types. One may suppose that modification results in an increase in the relative content of the surface groups that are necessary for chemisorption binding of the metal complex precursor.

The effect of γ -Al₂O₃ modification on the strength of interaction between metal complex and the support was studied using the GE method. Relying on platinum content determined in effluents, we plotted the dependences depicting the dynamics of complex desorption as the eluent passes through the column with the sample under investigation (Fig. 2). The mass balance of desorption experiment was checked (Table 1). Two desorption regions may be distinguished on the GE profile (see Fig. 2): these regions correspond to the removal of plat-

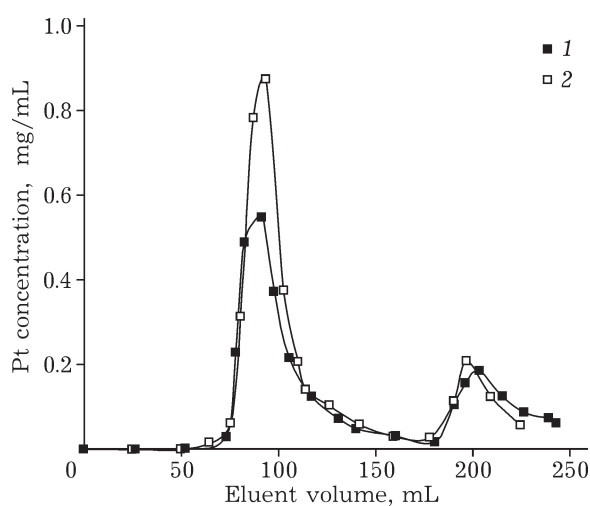


Fig. 2. GE profiles of the chloride complexes of platinum (IV) adsorbed on the surface of the support: 1 - 3% Al₂O₃/ γ -Al₂O₃; 2 - γ -Al₂O₃. Pt content in the initial samples: 1%.

inum complexes adsorbed on support surface with different strengths.

According to previous studies of the composition of effluents [3, 7, 16], easily desorbed forms (the first region of desorption) correspond to platinum complexes containing mainly chloride ligands. As the degree of hydrolysis of the complexes increases, their desorption hinders (the second region of desorption). In this situation, the most strongly hydrolysed compounds of averaged composition PtCl₂O₄ are so strongly bound with the surface of aluminium oxide (according to EXAFS data) that they are not desorbed at all under the conditions of GE.

The analysis of the data obtained suggests that the deposition of the precursor on modified support results in a decrease in the fraction of weakly bound complexes enriched with chloride. At the same time, the fraction of strongly bound non-desorbed forms of platinum increases by a factor of 2 (see Table 1). It was assumed in [3, 7] that the formation of the complexes so strongly bound with the surface of the support (internal sphere) occurs through the coordination mechanism:



This assumption is confirmed by the results of the studies of samples by means of TPR which is used to evaluate the strength of the interaction of metal complex with the support [23]. It is known that the stronger is binding of platinum complexes with the surface of aluminium oxide, the higher temperature is required for their reduction [4, 16]. Two regions of hydrogen absorption are observed on the obtained TPR profiles (Fig. 3). According to the data published in [4, 16], the peak of absorption with the maximum at a temperature of about 200 °C mainly corresponds to the reduction of weakly bound platinum forms, while strongly fixed forms absorb hydrogen in the region of 300–400 °C. The asymmetry of observed signals may be due to the differences in the chemical composition and strength of the interaction between the support surface and platinum compounds. This is confirmed by the results of desorption experiment (see Fig. 2) during which the fixed metal complexes were differentiated in composition and the strength of interaction with the support.

Deconvolution and integration of TPR signals allowed us to estimate the relative content

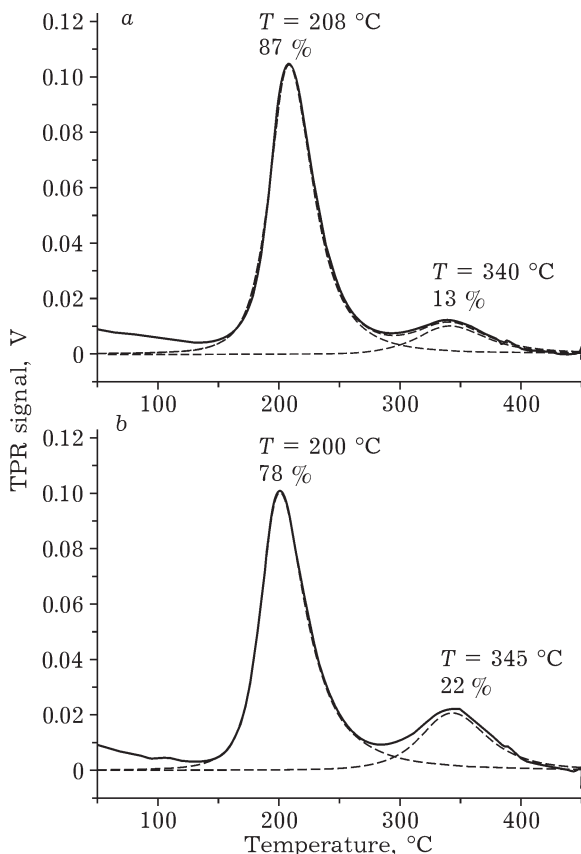


Fig. 3. TPR profiles of adsorbed complexes in the samples 1.0 % Pt/ γ -Al₂O₃ (a) and 1.0 % Pt/(3 % Al₂O₃/ γ -Al₂O₃) (b). Dash lines show the components of the contours obtained through their deconvolution using Pearson function IV.

of easily and difficultly reducible platinum compounds in the composition of the samples under study. The quantitative analysis of the results showed (see Fig. 3) that modification of the surface of the support leads to almost two-fold increase in the fraction of platinum forms strongly bound with the oxide surface; these forms are reduced in the high-temperature region. This result agrees with the GE data on a two-fold increase in the fraction of non-desorbed platinum forms in the composition of the modified sample (see Table 1).

The observed increase in the strength of the interaction between metal complex and the support in the case of support modification is likely due to an increase in the surface fraction of OH groups participating in the coordination with the precursor according to equation (4). These surface groups may be terminal hydroxyl groups that are the most basic groups due to

decreased Al–O bond energy in comparison with bridging groups [24, 25].

Dispersity of platinum particles in the samples reduced in TPR mode (the mass fraction of platinum 1.0 %) was determined by means of chemisorption of carbon monoxide. We did not reveal any substantial changes in the dispersity of the deposited metal during support modification; dispersity was conserved at a level of 73–75 %.

Effect of the deposition of oxide aluminium compounds onto γ -Al₂O₃ on the catalytic properties of the formed platinum centres

The effect of the changes in the state of the functional coating of the support on the catalytic properties of the ready catalysts Pt/Al₂O₃ was studied in model reactions of propane dehydrogenation in the flow mode and the transformations of *n*-hexane in the pulsed mode.

Propane dehydrogenation was chosen as the test reaction to characterize the catalytic properties of metal centres. As a rule, the target reaction of propylene formation on platinum is accompanied by the side processes of cracking, isomerization, oligomerization and coke formation proceeding mainly under the effect of the acid centres of the support [26, 27]. To suppress side reactions and increase the selectivity of propylene formation, the support is modified by introducing alkaline and alkaline earth metals. This not only suppressed the acid centres of the support but also provides platinum dispersity necessary for the achievement of high selectivity of dehydrogenation [27]. In addition, the addition of a second metal has become a common practice in the preparation of aluminoplatinum catalysts of dehydrogenation. The introduction of such metals as Au [28], Zn, Ce [29], Sn, Mo [26] allows one to increase the dispersity of platinum due to its dilution during the formation of the alloy, and also this allows one to modify the electronic state of active centres.

The results of the studies of samples prepared by us 0.50 % Pt/ γ -Al₂O₃ and 0.48 % Pt/(3 % Al₂O₃/ γ -Al₂O₃) in propane dehydrogenation are presented in Fig. 4 showing the dependencies of transformation degree, selectivity of propylene formation and the products of propane cracking (methane, ethane and ethyl-

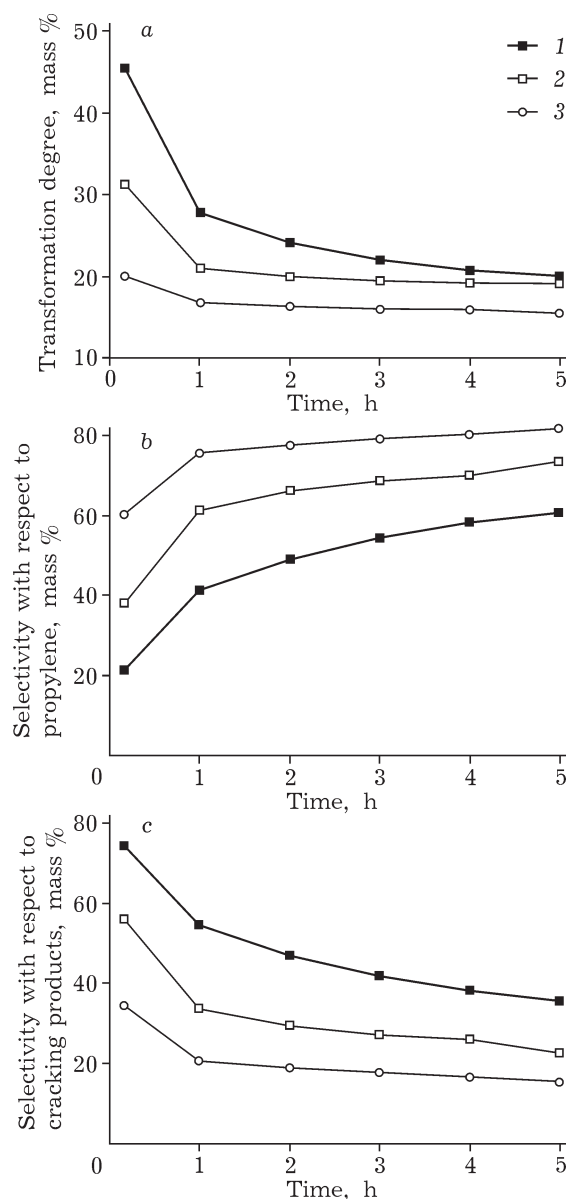


Fig. 4. Results of catalytic tests in propane dehydrogenation at a temperature of 550 °C in the flow mode: *a* – dependence of propane transformation degree on time, *b* – dependence of the selectivity of propylene formation on time, *c* – dependence of the selectivity of the formation of cracking products on time; 1 – 0.50 % Pt/ γ -Al₂O₃; 2 – 0.48 % Pt/(3 % Al₂O₃/ γ -Al₂O₃); 3 – 0.48 % Pt/ γ -Al₂O₃ after GE.

ene) on time. A decrease in the activity of the studied catalyst samples during the tests (see Fig. 4, *a*) is most clearly pronounced at the start of the experiment and can be due to partial deactivation of metal centres. After 305 h of experiment, the steady regime is observed; the activity does not change substantially with time.

The change of the state of functional coating of support surface during modification leads to a decrease in propane conversion degree at the beginning of the experiment (see Fig. 4, *a*) as a consequence of smaller cracking activity of the catalyst (see Fig. 4, *c*). A comparison between the samples under the steady conditions showed that, for the comparable activity, the use of the modified support provided an increase in the selectivity of propylene formation by 10 mass % (see Fig. 4, *b*).

The results of preliminary studies of the samples by means of H₂ chemisorption provide evidence of the same dispersity (90–96 %) of platinum particles in the modified support. In this connection, the observed difference in catalytic properties may be due to the change of the state of supported platinum as a consequence of the fraction of strongly fixed non-desorbing forms in the case of modified support. Indeed, the tests of the sample in which platinum is fixed only as non-desorbed forms (the introduction of GE stage) showed higher selectivity with respect to propylene (see Fig. 4, *b*, curve 3) and lower selectivity of the formation of products of propane cracking (see Fig. 4, *c*, curve 3).

This conclusion is confirmed by the results of [7, 16] where it was established that Pt/Al₂O₃ catalysts obtained from coordination-fixed precursor (using hydrolysed forms of the complexes), that is, enriched with platinum forms strongly bound with the surface of the support, possess a number of specific properties in comparison with traditional catalysts. They are characterized by high activity in cyclohexane dehydrogenation but decreased activity in hydrogenolysis of C–C bonds. The reason of the detected differences turned out to be different electronic states of supported platinum (for close dispersity values). In the catalyst obtained from coordination-bound precursor, the fraction of platinum in the oxidized state close to Pt²⁺ is substantially higher than that in the traditional sample [16].

Investigation of the systems 0.68 % Pt/ γ -Al₂O₃ and 0.65 % Pt/(3 % Al₂O₃/ γ -Al₂O₃) in the transformations of *n*-hexane within temperature range 250–450 °C (in hydrogen medium) did not reveal noticeable differences in their catalytic properties. The joint presence of dif-

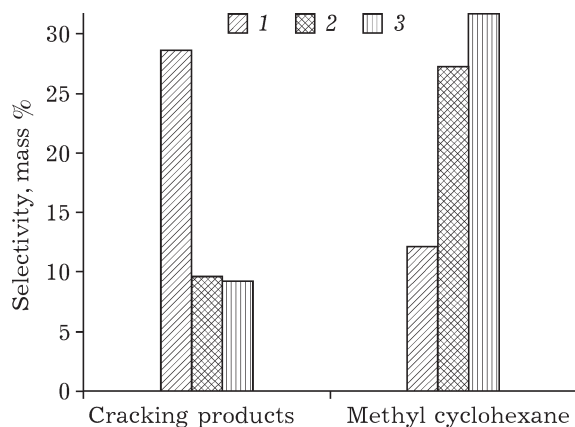


Fig. 5. Selectivity of the formation of cracking products and methylcyclopentane in the transformations of *n*-hexane within temperature range 320–390 °C for 20 % conversion degree: 1 – 0.68 % Pt/ γ -Al₂O₃; 2 – 0.23 % Pt/ γ -Al₂O₃ after GE; 3 – 0.49 % Pt/(3 % Al₂O₃/ γ -Al₂O₃) after GE.

ferent forms of deposited platinum (easily and difficultly reducible ones) in the case of rather high total platinum content seems not to allow us to differentiate the catalytic properties of these forms in the reaction under consideration and thus does not allow us to detect the effect of support modification.

At the same time, the samples obtained using strongly fixed forms (GE stage) are characterized by low selectivity of the formation of cracking products and the high selectivity of the formation of methylcyclopentane. With an increase in the fraction of these forms as a result of support modification the selectivity with respect to methylcyclopentane increases; so does its concentration in the products of *n*-hexane isomerization (methylpentanes) (Fig. 5). For example, in the products of *n*-hexane transformation within temperature range 320–390 °C with the conversion degree of 20 %, the following concentrations of methylcyclopentane were established (mass %): 0.68 % Pt/ γ -Al₂O₃ 18.7, 0.23 % Pt/ γ -Al₂O₃ (after GE) 36.2, 0.49 % Pt/(3 % Al₂O₃/ γ -Al₂O₃) (after GE) 50.2.

The observed difference in the catalytic properties may be explained by increased dehydrogenating activity, which is due to the higher fraction of platinum forms strongly bound with the modified support surface. It is known [30] that an increase in hydrogen content in reaction medium promotes the formation of methylcyclopentane in comparison with

other products of isomerization as a consequence of the prevailing role of the mechanism of C₅ cyclization in alkane transformations. An increase in the dehydrogenating activity of the modified catalyst sample obtained by us, exhibited as an increase in the selectivity of propylene formation during propane dehydrogenation (see Fig. 4) allows one to increase hydrogen concentration in the reaction system. This may explain an increase in the fraction of methylcyclopentane among the products of *n*-hexane isomerization in the case when the modified sample is used.

CONCLUSION

Thus, a change in the ratio of functional groups on γ -Al₂O₃ surface by modification with oxalate complexes of aluminium caused a 1.5-fold increase in the amount of adsorbed platinum in chloride complexes. This caused an increase in the fraction of strongly bound (internal-sphere) platinum compounds that are characterized by higher reduction temperature. An increase in the contribution from the coordination mechanism into precursor binding with the support is likely to be connected with an increase in the fraction of surface OH groups necessary for the formation of internal-sphere complexes.

An increase in the relative content of strongly bound platinum forms as a result of the modification of γ -Al₂O₃ surface affected the catalytic properties of the system Pt/Al₂O₃. Thus, we observed an increase in the content of methylcyclopentane in the products of *n*-hexane isomerization and an increase in the selectivity of propylene formation during propane transformation.

The principles of regulation of the state of support surface may be useful for a more thorough investigation of the regularities of the formation of active centres at the stage of impregnation for the synthesis of other supported metal catalysts of adsorption type.

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