

## CATALYSIS IN PETROLEUM REFINING INDUSTRY

# Characteristics and Catalytic Activity of Platinum Reforming Catalysts Based on Aluminum Oxide Modified by Organic Acids

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**Abstract**—The effect of treating aluminum oxide with organic acids (acetic acid, oxalic acid) on the dispersity, composition, and catalytic properties of the platinum sites of reforming catalysts is investigated. It is established that due to the high number of support defects, a Pt/Ox-Al<sub>2</sub>O<sub>3</sub> sample prepared on the basis of aluminum oxide treated with oxalic acid solution has the highest activity. The role the acid modification of a support plays in the formation of charged atoms of platinum, resulting in an increase of catalytic activity, is established.

**Keywords:** *n*-heptane reforming, Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalysts, surface defects

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## INTRODUCTION

The state of deposited platinum and the size of its particles, and thus the catalytic properties of the Pt/γ-Al<sub>2</sub>O<sub>3</sub> system, are determined by the strength of the interaction between the precursor of active component and the support. This interaction depends not only on the chemical composition of the precursor, but on the nature of the surface adsorption sites as well [1–7]. The adsorption sites of γ-Al<sub>2</sub>O<sub>3</sub> are hydroxyl groups and Lewis acid sites (LASs). The relative content of functional groups on the oxide's surface and their strength are mainly determined by the surface defects of the support.

It is known that most of the surface defects of γ-Al<sub>2</sub>O<sub>3</sub> form upon the dehydroxylation of its surface at temperatures above 300°C [8]. The number of defects grows due to the ions of the hydroxyl groups of the support being exchanged for the anions of acids, the removal of which produces additional surface defects that are able to adsorb the precursor of active component. In addition, treating the support with solutions of organic acids changes the acidity and distribution of its acid sites in terms of strength [9].

The aim of this work was to study the effect of surface defects of a support on the electronic state of platinum and the catalytic properties of the active phase of Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalysts in the reaction of *n*-heptane dehydrocyclization.

## EXPERIMENTAL

### *Support Preparation*

Spherical γ-Al<sub>2</sub>O<sub>3</sub> (Sasol Germany GmbH) with granules 1.6 mm in diameter was used as the initial support. The content of impurities in the aluminum oxide used in this work was the following (wt %): Na<sub>2</sub>O, 0.017; Fe<sub>2</sub>O<sub>3</sub>, 0.001.

### *Treatment with Acids*

Each spherical support was calcined at 600°C and held under vacuum for 15 min to remove all air from the inner volume of its pores to prevent its destruction upon wetting and preserve its strength and textural characteristics. A solution of oxalic acid was then poured onto aluminum oxide in a calculated ratio of 3 wt % (COOH)<sub>2</sub> to the weight of the support. The volume of the solution was calculated using a moisture capacity of 1.25 mg/g. The aluminum oxide was held in an acid solution for 1 h and dried in a drying oven for 1 h at 120°C.

The γ-Al<sub>2</sub>O<sub>3</sub> was similarly impregnated with 1 M CH<sub>3</sub>COOH solution in a calculated ratio of 4.5 wt % to the weight of the support.

The supports were calcinated inside a glass reactor in a flow of dried air at atmospheric pressure and 500°C for 1 h.

### *Preparing the Catalysts*

The active component (platinum) was deposited on the organic acid-modified calcined carrier in two stages. In the first stage, the aluminum oxide was treated with a solution of hydrochloric acid in a calculated ratio of 2.5 wt % to the weight of the carrier. Each support sample was held under vacuum for 20 min, and the calculated amount of HCl solution was added to it. It was then kept at room temperature for 30 min, after which the flask with the carrier was placed in a water bath and heated to 75°C for 30 min (hot impregnation). After hot impregnation, the resulting sample was separated from the solution and immediately subjected to the second stage, platinum deposition. The chlorine content of each solid sample was controlled via X-ray fluorescence.

H<sub>2</sub>[PtCl<sub>6</sub>] was sorbed from an excess of aqueous solution (Al<sub>2</sub>O<sub>3</sub> : solution weight ratio, 1 : 5) with no competitors at room temperature for 30 min, and then held in a water bath at 75°C for 60 min. This time ensured the sorption of most of the metal complex with no appreciable dissolution of aluminum oxide in the acidic medium. The concentration of the solution was selected from a calculated ratio of 0.5 wt % Pt to the weight of the support. Once dried at 120°C, the catalysts were calcined in a flow of dried air at 500°C for 1 h and reduced in a flow of dried hydrogen at 500°C for 2 h.

### *Thermogravimetry (TG)*

Thermal decomposition was investigated up to a temperature of 1000°C by means of TG using an STA-449C thermal analyzer (Netzsch) in a gas flow of 20 vol % O<sub>2</sub> in argon. The heating rate was 10°C/min.

### *X-ray Diffraction (XRD)*

The samples were subjected to XRD on a D8 Advance X-ray diffractometer using monochromatized CuK $\alpha$  radiation. ICDD databases (version PDF-2 of 2006) were used to interpret the obtained diffractograms. The diffraction spectra were processed using the EVA (Bruker) and Origin 6.0 software. Semiquantitative analysis was performed with the EVA software using data on the relative intensities and values of the corundum numbers from the database cards of powder diffraction. The size of the crystallites was determined using the Selyakov–Scherrer formula.

### *Textural Characteristics*

Nitrogen adsorption-desorption isotherms were obtained at 77.4 K on a Sorptomatic-1900 instrument (CarloErba). The specific surface areas were calculated by means of BET ( $S_{\text{BET}}$ ) in the range of equilibrium relative nitrogen vapor values when  $P/P_0 = 0.05$ –0.33 according to the adsorption isotherm. The total

adsorption volume of pores ( $\Sigma V_p$ ) was determined from the value of nitrogen adsorption when  $P/P_0 = 0.996$ ; the density of adsorbed nitrogen was assumed to be equal to the density of the normal liquid (the molar volume of liquid N<sub>2</sub> is 34.68 cm<sup>3</sup>/mol).

The Barrett–Joyner–Halenda approach was used to obtain the differential characteristics, i.e., the pore size distribution curves (PSDCs) [10].

### *Inductively Coupled Plasma Optical Emission Spectroscopy*

The content of Pt in the obtained catalysts was determined using a Varian-710ES atomic emission spectrometer (Agilent Technologies) with inductively coupled plasma. The arithmetic mean value of three parallel determinations was taken as the result of analysis. The relative standard deviation characterizing the reproducibility of the analysis did not exceed 0.02.

### *Temperature-Programmed Reduction of H<sub>2</sub> (TPR H<sub>2</sub>)*

The evolution of hydrogen absorption was investigated on an AutoChem II 2920 precision analyzer (Micromeritics) equipped with a thermal conductivity detector (TCD). Prior to each experiment, the samples were dried for 2 h in an air flow at a temperature of 200°C, followed by cooling to room temperature in an air flow. The experiments were performed with a mixture of 10 vol % H<sub>2</sub> in argon (flow rate, 25 mL/min) in the temperature range of 35–500°C at a furnace heating rate of 10°C/min, and each sample was held at the maximum temperature for 1 h.

### *O<sub>2</sub>/H<sub>2</sub> Titration and O<sub>2</sub> Chemisorption*

The dispersion of the reduced catalysts was determined by means of adsorption according to the results from oxygen–hydrogen titration. The number of surface atoms of platinum Pt<sub>s</sub> was calculated with allowance for the percentage of deposited metal and its dispersion.

The use of our adsorption technique [11] allowed us to quantify the platinum atoms in different degrees of oxidation. The approach is based on the ability of ionic platinum to form strong  $\sigma$  donor bonds with water, while atoms of metallic platinum (Pt<sup>0</sup>) do not interact with it. Ionic platinum was therefore designated Pt <sup>$\sigma$</sup> . The numbers of atoms in the Pt <sup>$\sigma$</sup>  state and the metallic (Pt<sup>0</sup>) state were determined using the data from measuring oxygen adsorption in two experiments. In the first experiment, the total number of Pt<sub>s</sub> atoms was determined by familiar means. In the second, the number of Pt<sup>0</sup> atoms that did not react with water was determined, and the presence of pre-adsorbed water did not interfere with the chemisorption of oxygen.

### Catalytic Measurements

The catalysts were tested in a model *n*-heptane reforming reaction in a setup with an ideal flow isothermal reactor at temperatures of 460–520°C, a pressure of 0.1 MPa, a flow hourly space velocity from 8 to 14 h<sup>-1</sup>, and a hydrogen : hydrocarbon ratio of 5 : 1 (mol.). The hydrocarbon compositions of the products of the mixtures formed during the reforming process, were analyzed on-line using a gas chromatograph equipped with a capillary column and a flame ionization detector.

One criterion for activity was calculated on the basis of the obtained data: specific productivity according to aromatic hydrocarbons SP, g<sub>ar</sub>/(g<sub>cat</sub> h), defined as the amount of formed aromatic hydrocarbons, in grams per gram of catalyst per 1 h:

$$SP = \frac{VX_A\rho}{100m},$$

where  $X_A$  is the content of aromatic hydrocarbons in gaseous steam, wt %;  $\rho$  is the density of heptane, g/cm<sup>3</sup>;  $V$  is the flow rate of heptane, cm<sup>3</sup>/h; and  $m$  is the weight of the catalyst, g.

The characteristics at a temperature of 490°C were taken as the average SP value.

The values of the rate constants of the directions of *n*-heptane conversion were calculated from test results (aromatization,  $k_a$ ; cracking,  $k_c$ ). The selectivity of aromatization ( $S_a$ ) was determined as the ratio  $k_a/k_t$ , where  $k_t$  is the total constant of the rate of *n*-heptane conversion. An additional criterion of catalyst selectivity was the yield of stable catalizate at a certain content of aromatic hydrocarbons in it. The activation energy ( $E_a$ , kJ/mol) was calculated using data from catalytic experiments at temperatures of 460, 480, 500, and 520°C.

## RESULTS AND DISCUSSION

The effect of acid treatment of aluminum oxide on the physicochemical properties of supports was studied in this work. Anions of the chosen acids (acetic, oxalic) can be removed from a surface of aluminum oxide via calcination at temperatures above 300°C [9, 12].

Our samples were Al<sub>2</sub>O<sub>3</sub> (the initial unmodified aluminum oxide) and Ox-Al<sub>2</sub>O<sub>3</sub> and Ac-Al<sub>2</sub>O<sub>3</sub> (specimens modified with oxalic and acetic acids, respectively).

Table 1 shows the XRD data (phase compositions, calculated lattice parameters ( $a$ , Å), and size of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> crystallites ( $D$ , Å)) for the investigated samples. They indicate high phase purity (100%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and the optimum size of support primary crystallites (45 Å). The parameters of the crystalline structure of aluminum oxide modified with organic acids are identical to the parameters of the initial support.

**Table 1.** Characteristics of the crystalline structure of aluminum oxides

Sample	Phase	$a$ , Å	$D$ , Å
Al <sub>2</sub> O <sub>3</sub>	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$7.913 \pm 0.001$	46
Ac-Al <sub>2</sub> O <sub>3</sub>	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$7.913 \pm 0.001$	45
Ox-Al <sub>2</sub> O <sub>3</sub>	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$7.913 \pm 0.001$	45

**Table 2.** Characteristics of the porous structure of aluminum oxides

Sample	$\Sigma V_{\text{pore}}$ , cm <sup>3</sup> /g	$D_{\text{av}}^*$ , Å	$S_{\text{BET}}$ , m <sup>2</sup> /g
Al <sub>2</sub> O <sub>3</sub>	0.55	104	211
Ac-Al <sub>2</sub> O <sub>3</sub>	0.56	111	199
Ox-Al <sub>2</sub> O <sub>3</sub>	0.54	107	201

$$^*D_{\text{av}} = 4V_{\Sigma\text{pore}}/S_{\text{BET}}.$$

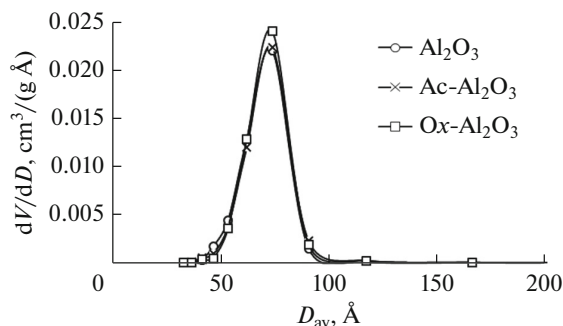
The characteristics of the porous structure of the investigated samples of aluminum oxide (Table 2) show that treating surfaces of aluminum oxide with solutions of acetic and oxalic acid does not appreciably alter the total volume of pores ( $\Sigma V_{\text{pore}}$ ), their diameter ( $D_{\text{av}}$ ), or their specific surface area ( $S_{\text{BET}}$ ).

Figure 1 shows that the pore size distribution curves of the initial and acid-treated aluminum oxide are similar and have maxima at 70 Å.

Treating surfaces of aluminum oxide with acetic and oxalic acids (in the concentrations used in this work) thus has no effect on the characteristics of crystalline and porous structures, indicating that such modification affects only the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The differential thermogravimetric (DTG) curves of the investigated aluminum oxide samples are presented in Fig. 2.

For all samples, the mass loss values at temperatures of up to 200°C are due to the removal of physically adsorbed water. The DTG curves differ appreciably in a region of higher temperatures.



**Fig. 1.** Pore size distribution for aluminum oxide samples.

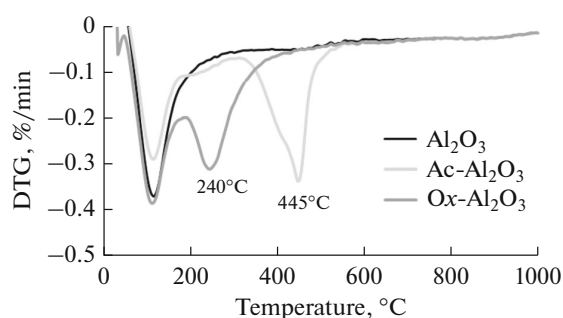


Fig. 2. DTG curves of aluminum oxide samples.

The mass loss of the initial  $\text{Al}_2\text{O}_3$  during calcination, calculated from the DTG curves in the temperature range of 200–500°C, were 1.62 wt %. A 3–4 wt % increase in mass loss upon calcination in an air flow is observed for the samples treated with organic acids. This was due to the decomposition of anions of organic acids on a surface of aluminum oxide with the release of  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ , along with the removal of surface  $\text{OH}^-$  groups.

According to the literature data, oxalic acid decomposes at 200°C, followed by the formation of formic acid and  $\text{CO}_2$  [12, 13]. Formic acid decomposes into  $\text{H}_2\text{O}$  and  $\text{CO}$  at higher temperatures. The maximum rate of  $\text{Ox-Al}_2\text{O}_3$  decomposition observed at 240°C (see Fig. 2) could be due to the decomposition of oxalic acid deposited on  $\gamma\text{-Al}_2\text{O}_3$ .

Acetic acid decomposes at elevated temperatures (400–450°C) in the presence of aluminum oxide catalyst [14]. We may therefore assume that for the  $\text{Ac-Al}_2\text{O}_3$  sample, the maximum of the rate of mass loss at a temperature of 445°C corresponds to the decomposition of acetic acid deposited on the aluminum oxide. The temperature maxima of the rate of organic aluminum salt decomposition agree with the literature data.

According to the TG data, the oxidation calcination of aluminum oxide samples at 500°C led to the full decomposition of organic acids on the aluminum oxide surface and the formation of pure  $\text{Al}_2\text{O}_3$ .

According to A.A. Lamberov et al. [9], the acidity of a support increases after acidic modification. The

change in distribution of acid–base sites on a surface of aluminum oxide is associated with the chemical interaction between an acid and aluminum oxide, as a result of which insoluble basic salts of aluminum form on the surface at the stage of heat treatment. In this work, aluminum oxide was modified with solutions of acids of low concentration (e.g., 0.625 mol/L for acetic acid). We may assume that in analogy with the data in [9], changes occur in a quantity of medium-strength LASs that probably affect the catalytic characteristics of the investigated catalyst samples.

#### Studying the Adsorption Properties of Catalysts via $\text{H}_2$ TPD

The platinum content in the investigated samples was 0.48–0.49 wt % (Table 3); for chlorine, it was 1.2 wt %. The patterns of the reduction of catalysts of 0.5 wt %  $\text{Pt/Al}_2\text{O}_3$  calcined at 500°C were studied by means of TPR. The TPR profiles (Fig. 3) show two regions of hydrogen absorption: low-temperature (200°C) and high-temperature (340°C). Modifying the support's surface raised hydrogen absorption in the high-temperature region to 20%. This accounts for the forms of platinum bonded strongly to the oxide surface [15, 16].

The fraction of platinum forms bonded strongly to the support was higher in the support sample treated with oxalic acid, due probably to the higher surface defectiveness, compared to the catalysts deposited on the initial support and treated with acetic acid.

Since the surface hydroxyl groups have a certain distribution according to the strength of basicity, we might expect that oxalic acid, whose dissociation constant (by the first stage) exceeds that of acetic acid, would be adsorbed less selectively upon full ion exchange. As a result, most of the hydroxyl groups of a  $\gamma\text{-Al}_2\text{O}_3$  surface, which are usually stable at the temperatures of preliminary treatment, will be replaced by acid anions upon the full adsorption of oxalic acid, and this will produce the greatest number of surface defects.

It was shown by MAS NMR  $^{27}\text{Al}$  [17], EXAFS [18], and high-resolution transmission electron microscopy [17, 18] that in addition to hydroxyl groups, the coordination-unsaturated cations of aluminum play a role in the adsorption of chloride complexes of platinum (IV)

Table 3. Dispersity and composition of the platinum sites of 0.5 wt %  $\text{Pt/Al}_2\text{O}_3$  catalysts

Sample	Platinum content, wt %	Dispersity of platinum, %	Quantity of surface $\text{Pt}_S$ , $\mu\text{mol/g cat.}$	
			$\text{Pt}^\sigma$	$\text{Pt}^0$
$\text{Pt/Al}_2\text{O}_3$	0.49	65	15.17	1.14
$\text{Pt/Ac-Al}_2\text{O}_3$	0.48	80	18.70	0.98
$\text{Pt/Ox-Al}_2\text{O}_3$	0.48	78	19.19	0

and the subsequent formation of the platinum oxide phase. The defect sites of  $\gamma$ - $\text{Al}_2\text{O}_3$  surfaces—five-coordinated Al ions—play a direct role in this. The authors of [18] showed that the strong interaction between supported platinum and the coordination-saturated surface sites of aluminum oxide prevents the agglomeration of particles.

#### Dispersity and Charge State of Pt

As was noted in [19], surface atoms of the metal in  $\text{Pt}/\text{Al}_2\text{O}_3$  catalysts can be in two states ( $\text{Pt}^0$  and  $\text{Pt}^\sigma$ ) that are characterized by different properties. Ionic forms of platinum ( $\text{Pt}^\sigma$ ) represent low-ligand clusters of platinum—systems of several metal atoms with degrees of platinum oxidation ranging from +1 to +2, formed due to electronegative chlorine, oxygen, sulfur atoms present in the coordination sphere of platinum.

$\text{O}_2$ - $\text{H}_2$  titration was used to determine the dispersity of surface atoms in particles on unreduced platinum. Prior to measuring adsorption, samples of chloride complexes of platinum fixed on aluminum oxide with different degrees of defectiveness were pretreated via calcination in a flow of dried oxygen at  $500^\circ\text{C}$  with subsequent reduction of the oxide forms of platinum in a hydrogen flow at  $500^\circ\text{C}$ .

Table 3 shows that as a result of the reduction of platinum complexes, the catalyst samples were characterized by higher dispersities of platinum: 65–80%. For  $\text{Pt}/\text{Al}_2\text{O}_3$  catalysts, the fraction of platinum sites in the charged state was 93% of the total number of active sites available for reaction. Samples prepared on supports treated with organic acids were characterized by higher proportions of  $\text{Pt}^\sigma$  sites: 95 and 100% for acetic and oxalic acids, respectively.

Our assumption that the defectiveness of aluminum oxide affects the composition of platinum catalysts for reforming was thus confirmed.

#### Catalytic Tests

The composition of platinum sites affects the catalytic behavior of catalysts. A typical model reaction for testing the catalytic properties of supported platinum is the dehydrocyclization of *n*-heptane ( $460$ – $520^\circ\text{C}$ ).

Samples of catalysts with a platinum content of 0.5 wt % were studied. Before any catalytic measure-

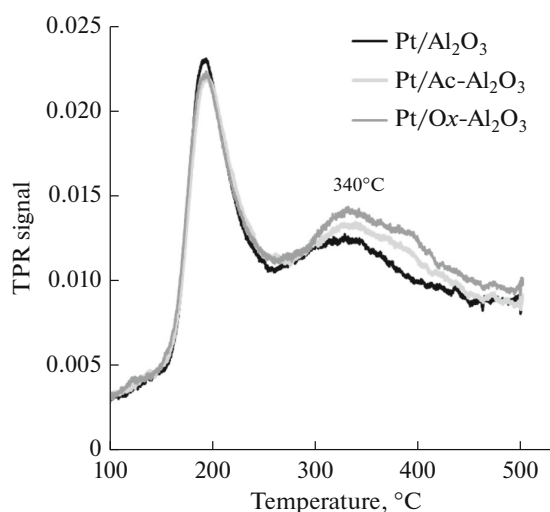


Fig. 3. TPR profiles of 0.5 wt %  $\text{Pt}/\text{Al}_2\text{O}_3$  samples.

ments, the samples of catalysts were preliminarily calcined at  $500^\circ\text{C}$  and reduced at  $500^\circ\text{C}$ . The results from our catalytic tests of the catalyst samples are shown in Table 4.

From our data, we can see that the introduction of acid at the stage of support synthesis of changes the activities of the catalysts. The highest SP was displayed  $\text{Pt}/\text{Ox-Al}_2\text{O}_3$  (on average,  $3.35 \text{ g}_{\text{ar}}/(\text{g}_{\text{cat}} \text{ h})$ ), and the lowest SP was displayed by  $\text{Pt}/\text{Al}_2\text{O}_3$  (on average,  $2.93 \text{ g}_{\text{ar}}/(\text{g}_{\text{cat}} \text{ h})$ ).

Our results on sample activity agree with data shown in Table 3 on the degree of platinum dispersion and the number of  $\text{Pt}^\sigma$  sites in a reforming catalysts.

Table 4 shows that the  $\text{Pt}/\text{Al}_2\text{O}_3$  sample displayed the highest selectivity of aromatization in the process of *n*-heptane conversion. The lowest selectivity  $S_a$  was displayed by the  $\text{Pt}/\text{Ox-Al}_2\text{O}_3$  sample. The highest rate of conversion ( $X = 85.7\%$ ) and the lowest yield of stable catalizate ( $W = 84.2 \text{ wt } \%$ ) were obtained on this sample. This can be explained by the fraction of adverse reaction growing as a result of the change in the acidity of the modified support's surface, particularly in the cracking of *n*-heptane.

Table 4. Catalytic properties of  $\text{Pt}/\text{Al}_2\text{O}_3$  catalysts\*

Sample	$\text{SP}_{490}, \text{g}_{\text{ar}}/(\text{g}_{\text{cat}} \text{ h})$	$S_a$	$E_a, \text{kJ/mol}$	$X, \%$	$W, \text{wt } \%$
$\text{Pt}/\text{Al}_2\text{O}_3$	2.93	0.60	137.4	80.1	88.0
$\text{Pt}/\text{Ac-Al}_2\text{O}_3$	3.27	0.57	129.1	80.0	87.2
$\text{Pt}/\text{Ox-Al}_2\text{O}_3$	3.35	0.54	99.7	85.7	84.2

\*SP is the specific productivity,  $S_a$  is the selectivity of aromatization,  $E_a$  is the activation energy,  $X$  is the conversion, and  $W$  is the stable catalizate yield.

When using the catalyst synthesized on the basis of the unmodified support, activation energy  $E_a$  was 137.4 kJ/mol (see Table 4). However, using the support treated with organic acids to prepare catalysts led to the formation of active sites that are characteristic of lower activation energies. The differences in energy lead us to assume its mechanism changes when Pt<sup>σ</sup> sites participate in the reaction of *n*-heptane dehydrocyclization.

According to the results from our catalytic tests, the highest values of activity were shown by Pt/Ox-Al<sub>2</sub>O<sub>3</sub> catalyst prepared on γ-Al<sub>2</sub>O<sub>3</sub> and treated with oxalic acid. The dispersity of the platinum in the sample was 78%. The Pt/Al<sub>2</sub>O<sub>3</sub> sample with lower activity was characterized by a lower dispersity of platinum (65%). The fraction of charged platinum was also higher in the Pt/Ox-Al<sub>2</sub>O<sub>3</sub> catalyst. According to the literature data [16], the electron-deficient forms of Pt that facilitate high activity in the target reactions of reforming are adsorbed in the places where defects are localized. The data obtained during our catalytic tests can thus be considered confirmation of an increase in the degree of a support's surface defectiveness as a result of treatment with solutions of oxalic and acetic acids.

### CONCLUSIONS

Treating surfaces of aluminum oxide with a solution of 3 wt % oxalic acid (4.5 wt % of acetic acid) has no effect on the parameters of the crystalline and porous structure of γ-Al<sub>2</sub>O<sub>3</sub>, but it ensures the formation of additional defects on the surfaces of modified supports.

Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalysts obtained on the basis of supports modified by acids are characterized by higher numbers of finely dispersed charged platinum sites than in the traditional catalyst.

The introduction of acid at the stage of preparing a support changes the catalytic properties of the catalyst in the reaction of *n*-heptane dehydrocyclization. Our Pt/Ox-Al<sub>2</sub>O<sub>3</sub> sample prepared on the basis of aluminum oxide treated with oxalic acid solution displayed the highest activity.

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