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Study of *n*-Hexane Isomerization on $Pt/SO_4/ZrO_2/Al_2O_3$ Catalysts: Effect of the State of Platinum on Catalytic and Adsorption Properties

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Abstract—The state of surface Pt atoms in the $Pt/SO_4/ZrO_2/Al_2O_3$ catalyst and the effect of the state of platinum on its adsorption and catalytic properties in the reaction of *n*-hexane isomerization were studied. The $Pt–X/Al_2O_3$ alumina–platinum catalysts modified with various halogens (X = Br, Cl, and F) and their mechanical mixtures with the $SO_4/ZrO_2/Al_2O_3$ superacid catalyst were used in this study. With the use of IR spectroscopy (CO_{ads}), oxygen chemisorption, and oxygen–hydrogen titration, it was found that ionic platinum species were present on the reduced form of the catalysts. These species can adsorb to three hydrogen atoms per each surface platinum atom. The specific properties of ionic platinum manifested themselves in the formation of a hydride form of adsorbed hydrogen. It is believed that the catalytic activity and operational stability of the superacid system based on sulfated zirconium dioxide were due to the participation of ionic and metallic platinum in the activation of hydrogen for the reaction of *n*-hexane isomerization.

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INTRODUCTION

The isomerization reactions of $C_4–C_6$ light alkanes are of considerable current interest. Catalysts that have been commonly used previously, such as aluminum chloride and liquid acids, do no meet environmental, corrosion, and other requirements. Therefore, they should be replaced by solid acids. Zeolites and metal oxides modified with SO_4^{2-} ions (primarily, SO_4/ZrO_2) belong to solid acids; they exhibit superacid properties and actively isomerize alkanes at a low temperature [1, 2]. However, although the selectivity of the process on SO_4/ZrO_2 is high, this system is less active than $Pt–Cl/Al_2O_3$. Moreover, this catalyst is rapidly deactivated with an irreversible loss of activity. The addition of platinum increases the activity of the SO_4/ZrO_2 catalyst and considerably enhances its stability in the reaction of $C_4–C_6$ paraffin isomerization [3], which is usually performed in an atmosphere of hydrogen at 150–250°C. It is evident that, under these conditions, platinum can undergo reduction up to the metal. The XPS data indicate that only 15% Pt occurred in a metal state, and the major portion remained oxidized even upon reduction with hydrogen at 350°C [4]. According to other data, which were also obtained by XPS, the main state of Pt was zerovalent particles covered with a PtS layer after the reductive treatment of the catalyst. These special features were used to explain the results of the extremely low chemisorption activity of Pt in the $Pt/SO_4/ZrO_2$ sulfated system [5, 6]. The IR-spectroscopic studies of the state of Pt with the use of CO adsorption also demonstrated that platinum did not entirely occur in a metal state and charged platinum particles were formed in the course of reduction of the $Pt/SO_4/ZrO_2$ system [7, 8].

There is no general agreement among authors as to the role of various states of platinum in sulfate–zirconia catalysts in isomerization [5–13]. The high stability of platinum-containing catalysts was related to the activation of hydrogen on platinum metal and the hydrogenation of coke precursors [5]. The modification effect was explained by the formation of new proton sites [4, 13] as a result of the interaction of hydrogen with platinum. A reaction scheme of *n*-hexane isomerization was proposed [9–11, 13], in which platinum was considered as a supplier of hydride ions to a carbocation isomerized at an acid site. However, no experimental evidence for the formation of hydrides on platinum was presented in the cited publications. Published data on the state (oxidation number or charge) of surface platinum atoms are considerably different [4–8, 10]. There are almost no published data concerning the adsorption of hydrogen, which is an important participant of isomerization reaction in

Table 1. Characteristics of the $SO_4/ZrO_2/Al_2O_3$ acid catalyst

Chemical composition, wt %			Texture characteristics			X-ray diffraction characteristics		
SO_4	ZrO_2	Al_2O_3	V_{pore}, cm^3/g	S_{BET}, m^2/g	R^*_{eff}, nm	Phase composition of ZrO_2^{**}, wt %		Crystallite size of t-ZrO_2^{**}, nm
						t-ZrO_2^{**}	m-ZrO_2	
6	70	24	0.34	110	5	95	5	6

* R_{eff} is the effective pore radius.

** t-ZrO_2 and m-ZrO_2 are the tetragonal and monoclinic modifications, respectively.

the absence of which the activity of $Pt/SO_4/ZrO_2$ catalysts is unstable, on platinum.

Theoretical works devoted to the quantum-chemical studies of the state of a metal, in particular, Pt, in heterogeneous catalysts have been published recently [14–18]. These publications considered the nature of bifunctional catalysts in a new way. An alternative mechanism of alkane conversion was proposed without the participation of acid sites. The reactivity of Pt in zeolites was calculated using the density functional method [14, 15], and the possibility of converting alkanes adsorbed immediately on platinum particles was demonstrated. A special feature of these particles is the ability to adsorb hydrogen in ratios of $H/Pt > 1$ [17–19].

Ambiguous data on the state of Pt in sulfate–zirconia systems and its role in catalysis stimulated us to continue a study on the effect of the electronic state of surface Pt atoms on adsorption and catalytic properties in the reaction of *n*-hexane isomerization in an atmosphere of hydrogen.

In preliminary experiments with model catalysts as mechanical mixtures of an acid component (the $SO_4/ZrO_2/Al_2O_3$ catalyst) and a metal component (Pt on Al_2O_3 and SiO_2 supports), Smolikov et al. [20] found that catalysts with the oxidized platinum Pt^{2+} (systems based on $Pt–Cl/Al_2O_3$) exhibited high catalytic activity in *n*-hexane isomerization. The activity level of catalysts with only Pt^0 atoms (systems based on Pt/SiO_2) was incommensurably lower. A special feature of $Pt–Cl/Al_2O_3$ catalysts is the stabilization of Pt^{2+} ions as a $[PtO_xCl_y]$ surface complex [21].

In this work, we studied the effect of the electronic state of platinum on the adsorption of hydrogen and the activity of the $Pt/SO_4/ZrO_2/Al_2O_3$ superacid catalyst in the reaction of *n*-hexane isomerization in an atmosphere of hydrogen. To determine the effect of the state of Pt, we used model mixtures of the $SO_4/ZrO_2/Al_2O_3$ superacid catalyst with no platinum with metal components—the $Pt–X/Al_2O_3$ platinum catalysts (where X = Cl, Br, and F), from which platinum metal atoms were absent and the ionic state of platinum was characterized as Pt^{2+}.

EXPERIMENTAL

Preparation of Catalysts

Acid catalysts without platinum (the $SO_4/ZrO_2/Al_2O_3$ system) and with supported platinum ($Pt/SO_4/ZrO_2/Al_2O_3$), $Pt–X/Al_2O_3$ alumina–platinum catalysts with various halogens (Br, Cl, and F), and mechanical mixtures of the $SO_4/ZrO_2/Al_2O_3$ and $Pt–X/Al_2O_3$ catalysts in a weight ratio of 1 : 1 were used in this study.

The acid catalyst was prepared from an aqueous solution of $ZrO(NO_3)_2$ with a concentration of 90 g/l in terms of ZrO_2. The precipitation of zirconium dioxide hydrate was performed at 60–65°C on the addition of an ammonia solution to a zirconium salt solution until pH 10–11. The resulting precipitate was washed, dried at 120°C, and then treated with a 12% solution of sulfuric acid. Aluminum hydroxide as a binding agent was added to the predried material for molding and strengthening the support granules. The washed and dried (at 120°C) material was calcined at 650°C in a flow of dry air to obtain crystalline zirconium oxide. Zirconium dioxide in the acid catalyst after sulfation and calcination contained 95% of the t-ZrO_2 tetragonal phase (Table 1).

To prepare a sample of $Pt/SO_4/ZrO_2/Al_2O_3$, the acid catalyst was impregnated with chloroplatinic acid to obtain a 0.4 wt % platinum content of the prepared catalyst. Then, the sample was dried at 120°C and calcined at 450°C in a flow of dried air.

The alumina–platinum catalysts modified with Br, Cl, and F halogens ($Pt–X/Al_2O_3$) were prepared in accordance with the following procedure: γ-Al_2O_3 (total pore volume, 0.65 cm^3/g; BET specific surface area, 230 m^2/g; and effective pore radius, 7.0 nm) was used. The support was precalcined at 580°C and evacuated to remove air from pores in order to prevent the formation of cracks and a loss in the pore volume. Then, the support was impregnated with aqueous solutions of HBr, HCl, and HF acids to obtain uniform impregnation and homogeneous Pt distribution over the volume of support grains. Platinum was supported from an aqueous solution of H_2PtCl_6 and H_2PtBr_6 acids taken in amounts corresponding to platinum concentrations in the prepared catalyst at a level of 0.4–0.5 wt %. The support was impregnated with a platinum-containing acid for 1 h with an expo-

Table 2. Characteristics of the Pt–X/Al_2O_3 (X = Br, Cl, and F) and Pt/SO_4/ZrO_2/Al_2O_3 catalysts

Sample	Pt content, wt %	Training conditions	Dispersity of Pt, %
Pt-Br/Al_2O_3	0.44	O_2 500°C, H_2 500°C	91
Pt-Cl/Al_2O_3	0.47	O_2 500°C, H_2 500°C	100
Pt-F/Al_2O_3	0.42	O_2 500°C, H_2 500°C	100
Pt/SO_4/ZrO_2/Al_2O_3	0.40	O_2 450°C, H_2 270°C	16

sure at 70–75°C. The impregnated support was washed with distilled water to remove unsorbed platinum solution, dried at 120°C in air, and calcined at 500°C in a flow of dried air. Before use, the prepared samples were reduced with hydrogen at 500°C. Table 2 summarizes the characteristics of Pt–X/Al_2O_3 and Pt/SO_4/ZrO_2/Al_2O_3 samples.

Experimental Procedures

The catalytic studies of the reaction of *n*-hexane isomerization were performed in a flow system with an isothermal catalytic fixed-bed tube reactor and a thermocouple well arranged along the reactor axis. The catalyst loading in the reactor was 2 cm^3; the particle size was 0.25–0.75 mm.

Before loading into the reactor, the Pt–X/Al_2O_3 alumina–platinum catalysts were preactivated in an individual setup in a flow of purified hydrogen with a stepwise temperature increase to 500°C and kept for 1 h at this temperature. The SO_4/ZrO_2/Al_2O_3 acid catalyst was calcined at 650°C in a flow of dry air before preparing a mechanical mixture for catalytic tests. The further activation of catalysts (and mixtures) was performed immediately in the catalytic setup in a flow of purified hydrogen for 2 h at a temperature of 270°C. The catalytic reaction was performed at 140–400°C, a pressure of 1.5 MPa, an LHSV of 2 h^{-1}, and an H_2/*n*-C_6 molar ratio of 3 : 1.

The raw material, chemically pure *n*-hexane dried with molecular sieves NaX, was supplied with a dispensing pump to a T-shaped pipe for mixing with hydrogen and then to the reactor. The reaction products were analyzed on line using a Tsvet-800 chromatograph with a Petrocol DH 50.2 capillary column.

The mechanical mixtures were prepared in an agate mortar by mixing and grinding a metal component (Pt–X/Al_2O_3 catalysts) and an acid component (the SO_4/ZrO_2/Al_2O_3 catalyst) in a weight ratio of 1 : 1. Then, the resulting powder was pressed at 9 MPa and ground in a mortar, and a fraction of 0.25–0.75 mm was taken for catalytic tests.

The IR spectra were measured in the region of 4000–1000 cm^{-1} on a Shimadzu 8300 spectrophotometer equipped with a DRS-800 diffuse reflectance attachment. A resolution of 4 cm^{-1} was used with the averaging of 50–100 accumulated spectra. The intensity of the spectra was expressed in Kubelka–Munk units. Before spectroscopic studies, the samples placed in a movable cell, activated in a vacuum, and reduced in a special setup. The cell for spectroscopic measurements was made of quartz and equipped with a window of CaF_2. To study the state of platinum, CO (30 Torr) was added to the pretreated and evacuated samples (fraction of 0.25–0.75 mm) at a temperature of 25°C. After measuring the spectrum, the sample was evacuated at room temperature, and the spectrum was measured once again.

The H/D isotope exchange was studied on a Shimadzu 8300 spectrometer in the transmission mode with the use of a mixture containing 97 vol % isotope. The studies were performed in situ with the use of a movable cell. For this purpose, a freshly prepared and dried (at 120°C) sample was pressed without a binder to form a pellet with a density of 20 g/cm^3 and treated in oxygen and then in a vacuum at 450°C and the initial spectrum was measured. Thereafter, hydrogen was added to the cell at a pressure of 100 Torr and the spectra were measured while heating the sample in hydrogen from room temperature to 250°C in steps of 50 K. The isotope exchange was performed after cooling the samples with adsorbed hydrogen by adding a mixture with deuterium at room temperature followed by heating to 250°C in steps of 50 K with measurement of IR spectra.

An oxygen–hydrogen (O_2–H_2) titration and oxygen adsorption procedure [22, 23] was used for adsorption studies in order to evaluate the dispersion, the amounts of adsorbed oxygen and hydrogen, and the state of surface platinum atoms.

The phase composition of the catalysts was analyzed on a DRON-3 diffractometer using monochromated CuK_α radiation and a β-filter.

The pore structure parameters of the samples were measured on a Sorptomatic-1900 instrument using the isotherms of N_2 adsorption at 77 K.

RESULTS AND DISCUSSION

n-Hexane Isomerization

Table 3 and Figs. 1 and 2 summarize the results of the catalytic tests of superacid catalysts (SO_4/ZrO_2/Al_2O_3 and Pt/SO_4/ZrO_2/Al_2O_3), mixed

Table 3. Isomerization of *n*-hexane on $SO_4/ZrO_2/Al_2O_3$ and mixtures with $Pt–X/Al_2O_3$ (X = Br, Cl, and F)

Catalyst	*T*, °C	Conversion, %	Yield of hydrocarbons, wt %					Selectivity for *iso*-C_6, wt %
			$C_1–C_4$	*iso*-C_5	*n*-C_5	ΣDMB**	ΣMP**	
$SO_4/ZrO_2/Al_2O_3$	140*	89.5	5.3	1.3	0.3	40.2	42.5	92
	140	4.3	0	0	0	0.6	3.3	90
	160	5.9	0	0	0	0.8	4.8	95
	180	12.9	0.2	0	0.1	1.9	10.3	95
	200	11.6	0.4	0	0.2	1.7	9.3	94
	220	15.1	0.9	0.4	0	2.0	11.6	90
$Pt/SO_4/ZrO_2/Al_2O_3$	140	87.3	3.2	2.9	1.0	34.4	45.7	92
	160	87.0	2.0	0.5	0.1	29.9	53.6	96
	180	87.1	2.5	0.6	0.3	29.5	54.1	96
	200	86.9	5.4	1.4	0.4	26.2	52.9	91
	220	87.9	21.1	5.0	1.6	22.0	38.3	69
$SO_4/ZrO_2/Al_2O_3$ + $Pt\text{-}Br/Al_2O_3$	180	22.7	0.2	0.1	0	3.3	18.7	97
	220	53.8	2.8	1.0	0.1	8.2	41.4	92
	260	74.7	14.8	4.0	1.0	10.8	43.8	73
$SO_4/ZrO_2/Al_2O_3$ + $Pt\text{-}Cl/Al_2O_3$	180	30.7	0.3	0	0.1	4.9	24.9	97
	220	66.0	3.6	1.0	0.2	11.9	49.1	92
	260	83.5	23.3	4.7	1.4	13.4	40.5	65
$SO_4/ZrO_2/Al_2O_3$ + $Pt\text{-}F/Al_2O_3$	180	34.2	0.3	0	0.1	5.0	25.4	89
	220	68.0	3.6	1.0	0.2	12.1	50.1	91
	260	87.0	23.8	4.8	1.5	13.7	41.4	63

* Characteristics measured in a 10-min experiment; in the other experiments, the characteristics were measured after 30 min.
** DMB and MP refer to dimethylbutanes and methylpentanes, respectively.

systems ($SO_4/ZrO_2/Al_2O_3$ + $Pt–X/Al_2O_3$), and $Pt–X/Al_2O_3$ catalysts.

The $SO_4/ZrO_2/Al_2O_3$ system initially exhibited high catalytic activity in the reaction of *n*-hexane isomerization; the yield of hexane isomers after a 10-min experiment was 82.7% (Table 3). As the experiment time was increased to 30 min, activity characteristics considerably decreased. The yield of isomerization products at 140–160°C was about 4–5% at 90–95% selectivity (Table 3). An increase in the temperature to 220°C increased the yield of isomerization products to 12–13%; however, selectivity for isohexanes decreased because of an increase in the yield of cracking products.

The introduction of platinum into $SO_4/ZrO_2/Al_2O_3$ resulted in a considerable increase in the operational stability of the $Pt/SO_4/ZrO_2/Al_2O_3$ catalytic system. The yield of isomerization products was as high as 83.5–83.6% at 96% selectivity for isohexanes. The reaction products contained 2-methylpentane, 3-methylpentane, deep isomerization products (2,2- and 2,3-dimethylbutanes), and $C_1–C_5$ cracking products (Table 3). An increase in the isomerization temperature to 200°C affected only slightly process parameters: the yield of hexane isomers was retained at a level of 79 at 91% selectivity. The same dependence was also observed in cracking products: the yields of $C_1–C_4$ and C_5 products increased only slightly to 200°C. An increase in the temperature above 200°C considerably decreased the yield of isomers to 60.3%, and selectivity dramatically decreased to 69% because of the development of cracking reactions. Thus, the addition of platinum to the catalyst considerably increased conversion and the yield of isomers.

To determine the effect of the state of platinum on activity, we performed experiments on *n*-hexane isomerization on catalyst mixtures: a $Pt–X/Al_2O_3$ alumina–platinum catalyst was added to a low-activity $SO_4/ZrO_2/Al_2O_3$ acid component in a weight ratio of 1 : 1 (Fig. 1). Catalysts with various halogens (X = Br, Cl, and F) were specially chosen to change the state of a platinum site according to published data [21]. Before considering the experiments with mixtures, it is necessary to explain the choice of components for these mixtures. The $Pt–X/Al_2O_3$ (where X = Br, Cl,

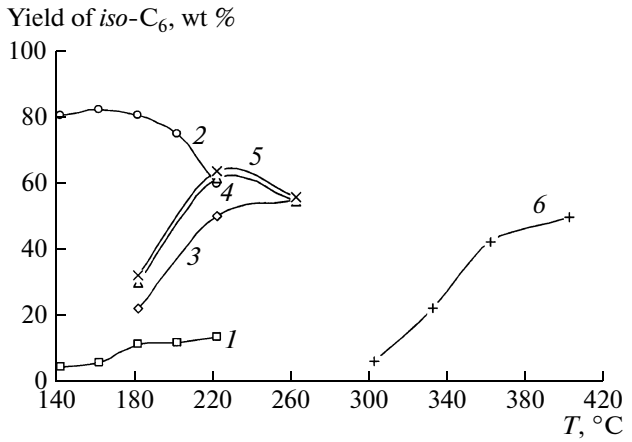

Fig. 1. The temperature dependence of the yield of hexane isomers for (*1*) $SO_4/ZrO_2/Al_2O_3$ and (*2*) $Pt/SO_4/ZrO_2/Al_2O_3$ catalysts and $Pt–X/Al_2O_3$ + $SO_4/ZrO_2/Al_2O_3$ mixtures (X = (*3*) Br, (*4*) Cl, and (*5*) F). (*6*) Data for a mixture of $Pt/SiO_2 + SO_4/ZrO_2/Al_2O_3$ were taken from [20].

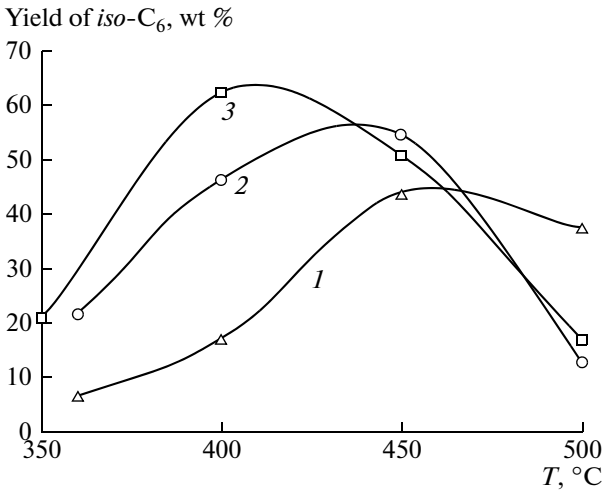

Fig. 2. The temperature dependence of the yield of hexane isomers for $Pt–X/Al_2O_3$ catalysts: X = (*1*) Br, (*2*) Cl, and (*3*) F.

and F) alumina–platinum systems themselves are active isomerization catalysts. Figure 2 shows the temperature dependence of the yields of hexane isomers obtained in this work on the above catalysts. For isomerization on alumina–platinum systems, optimum temperatures are higher than 400°C, which is characteristic of high-temperature isomerization in accordance with a bifunctional mechanism [24]. In a classical form, the bifunctional mechanism implies the independent actions of metal and acid sites. Previously [21, 22, 25, 26], it was found that, in the $Pt–X/Al_2O_3$ catalysts modified with chloride and bromide ions, Pt atoms were stabilized by chemical interaction with the surface sites of alumina—surface Al^{3+} cations (L refers to Lewis sites)—and halide ions to form the $[PtO_xX_y]$ surface complex. Thus, by introducing various halogen atoms into the catalyst, we purposefully changed the chemical composition of platinum-containing sites. Replacing chlorine by bromide or fluoride ions, we obtained considerable changes in the catalytic activity of the alumina–platinum samples (Fig. 2). The yield of hexane isomers reached maximum values of 40–45, 50–55, and 60–65% for catalysts in the order Br → Cl → F, respectively. The temperature range of maximum activity decreased in the same order. Thus, the experimental results suggest that, in terms of the bifunctional action mechanism, the state of platinum-containing sites in the $[PtO_xX_y]$ surface complexes exerted a considerable effect on the activity of the catalyst in the reaction of *n*-hexane isomerization: the activity of catalysts increased with increasing halogen electronegativity in the order Br → Cl → F. This is also evidenced by a decrease in the temperature of maximum activity from 450–470 to 390–420°C in the above order of catalysts.

Let us return to the results shown in Fig. 1 for mixed catalysts. In a preliminary study, Smolikov et al. [20] found that the mixtures containing an $SO_4/ZrO_2/Al_2O_3$ acid component and a Pt/SiO_2 catalyst, in which platinum occurred only in a metal state (Pt^0), exhibited activity over the temperature range of 300–400°C, that is, in the region close to that of high-temperature isomerization [24]. In the mixed catalysts based on Pt/Al_2O_3, which are active in a low-temperature isomerization region [20], ionic platinum species, which are stabilized as the $[PtO_xCl_y]$ complex in $Pt–Cl/Al_2O_3$ catalysts, should be present in addition to Pt^0 atoms.

As can be seen in Table 3, the mixed catalysts with ionic platinum occupy an intermediate position between the individual $SO_4/ZrO_2/Al_2O_3$ and $Pt/SO_4/ZrO_2/Al_2O_3$ superacid catalysts in terms of conversion and the yield of isomers. The addition of an acid component to the alumina–platinum catalyst shifts the reaction to the range of temperatures much lower than 380–420°C, which is characteristic of a classical bifunctional mechanism of isomerization on $Pt–X/Al_2O_3$ (cf. Fig. 2). The temperature range of a maximum yield of hexane isomers on the mixed catalysts containing $[PtO_xX_y]$ complexes is 200–240°C (Fig. 1). The experimental results indicate that the ionic state of Pt plays an important role in the catalysis of hexane isomerization both in the case of alumina–platinum catalysts (bifunctional catalysis) and in the presence of the $SO_4/ZrO_2/Al_2O_3$ superacid system. Mechanical mixtures with ionic platinum are active over a much lower temperature range, as compared with that for mixtures based on Pt/SiO_2 (Pt^0 metal atoms). However, a pronounced effect of the nature of a halogen is not observed in the mixed catalysts. It is likely that the mechanism of the reaction on mixed

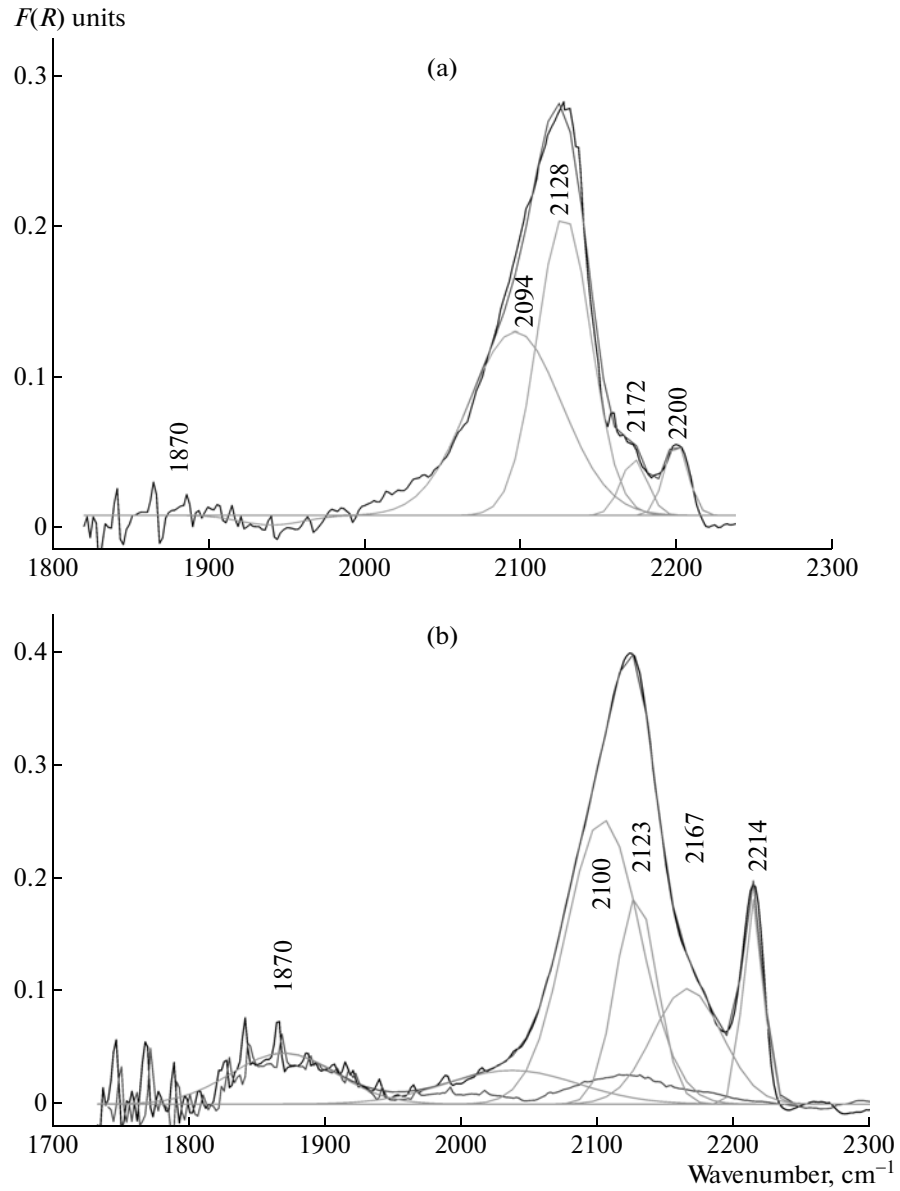

Fig. 3. Diffuse reflectance IR spectra of CO adsorbed on (a) $Pt–Cl/Al_2O_3$ and (b) $Pt–F/Al_2O_3$ reduced with H_2 at 500°C.

catalysts is different from the classical bifunctional mechanism, which is characteristic of alumina–platinum systems [24]; correspondingly, platinum plays another role in this case.

State of Platinum in the Catalysts

Figure 3 shows the IR spectra of CO adsorbed on alumina–platinum catalysts. After the deconvolution of the spectra, individual components manifested themselves as bands at 2094 and 2100 cm^{-1}, which can be attributed to platinum metal bearing a small charge δ^+. A distinctive feature of halogen-containing catalysts is the presence of absorption bands at 2123, 2128, 2167, and 2172 cm^{-1} due to CO adsorbed in a linear form on oxidized platinum sites in the IR spectra. We can conclude that platinum supported on aluminum oxide was incompletely reduced in the alumina–platinum catalysts used in this study even after training in H_2 at 500°C.

After the adsorption of CO on the $Pt/SO_4/ZrO_2/Al_2O_3$ catalyst reduced in H_2 at 270°C (Fig. 4), the spectrum exhibited absorption bands with maximums at 2099, 2116, 2151, and 2202 cm^{-1}. The last-named band is characteristic of CO complexes with Lewis acid sites (LASs) on the surface of $SO_4/ZrO_2/Al_2O_3$. The band at 2151 cm^{-1} can be ascribed to linear CO complexes with Pt ions, which can be the constituents of $(SO_3–O)–Pt$ surface complexes [7]. The frequencies of 2116 and 2099 cm^{-1} can

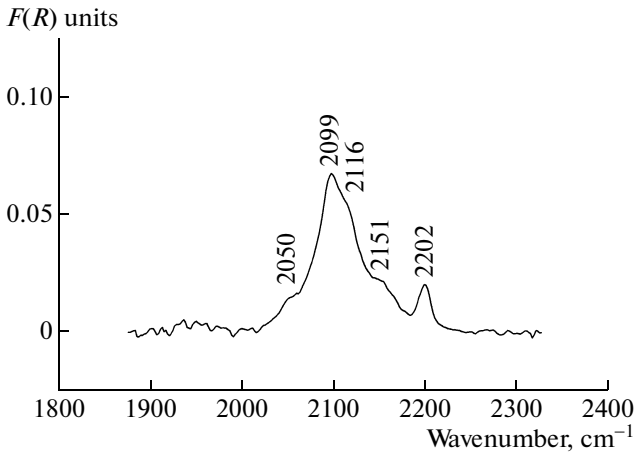

Fig. 4. Diffuse reflectance IR spectra of CO adsorbed on $Pt/SO_4/ZrO_2/Al_2O_3$ reduced at 270°C.

be attributed to the vibrations of CO adsorbed in a linear form on $Pt^{\delta+}$ and Pt^0 particles, respectively. A shift of the absorption band of adsorbed CO from 2070–2080 cm^{-1}, which are typical values of the metal, to 2099 cm^{-1} suggests platinum metal, which is strongly affected by SO_4/ZrO_2 acid sites [7, 8].

The above spectroscopic characteristics clearly indicate that ionic platinum was present in the test catalytic systems. In the alumina–platinum systems, ionic platinum was identified as the $[PtO_xX_y]$ complex bound to LASs. In the superacid catalyst, the ionic form of Pt hypothetically occurred in the neighborhood of Lewis sites as structures like $(SO_3–O)–Pt$ [7]. According to our data [21, 23], the $[PtO_xCl_y]$ surface complexes exhibited specific properties; in particular, they adsorbed hydrogen with the stoichiometry H/Pt = 2. It is likely that the high adsorption capacity of ionic platinum for hydrogen can explain the high catalytic activity of ionic platinum in the isomerization reaction in an atmosphere of hydrogen. If the reaction was performed in an inert gas (nitrogen or helium) atmosphere, rapid deactivation occurred in a few minutes analogously to the case that the acid component with no platinum was used for isomerization. Therefore, to explain the role of various states of Pt, we studied the adsorption properties of platinum in the $Pt/SO_4/ZrO_2/Al_2O_3$ and $Pt–X/Al_2O_3$ catalysts with the use of O_2 chemisorption and $(O_2–H_2)$ titration.

Adsorption Properties of Platinum in Catalysts

Previously [21–23], we successfully applied chemisorption and titration methods to study the adsorption properties of platinum ions in $[PtO_xCl_y]$ and $[PtO_xBr_y]$ complexes as the constituents of alumina–platinum catalysts for catalytic reforming. Table 4 summarizes the absorption of oxygen according to $(O_2–H_2)$ titration and O_2 chemisorption data, which were obtained for the catalysts in the determination of the dispersity (the number of surface atoms) of platinum in accordance with an adsorption procedure [22, 23]. Based on the adsorption data, we calculated the amounts of adsorbed hydrogen per surface platinum atom in each particular catalyst. A well-known rule, according to which the amount of oxygen consumed for titration is equal to the sum of the amounts of oxygen chemisorbed on platinum and consumed for the interaction with hydrogen adsorbed on platinum with the formation of water, was used for the calculations:

$$OT = OC + 1/2HC,$$

where OT is the consumption of oxygen in titration, (atom O)/(atom Pt_t); OC is the consumption of oxygen in chemisorption on platinum, (atom O)/(atom Pt_t); HC is the amount of chemisorbed hydrogen on platinum, (atom H)/(atom Pt_t) (here, Pt_t refers to the total number of platinum atoms in the catalyst).

The number of hydrogen atoms adsorbed by a surface platinum atom can be obtained by relating the values of H/Pt_t to the dispersity of platinum (in terms of a surface Pt_s atom). Data in Table 4 indicate that, in the series of $Pt–X/Al_2O_3$ catalysts, the ability of surface Pt atoms to adsorb hydrogen increased in the halogen order Br → Cl → F. It is well known that the acid properties of γ-Al_2O_3 were enhanced in the same order upon the addition of halogens [24]. For the Pt/Al_2O_3 systems modified with weak- and medium-acidity halogens (bromine and chlorine), specific chemisorption values were similar: $H/Pt_s = 1.89–2.00$. Upon modification with fluorine, which is a strong-

Table 4. Adsorption characteristics of Pt in catalysts: dispersity, oxygen consumption upon chemisorption (OC) and titration (OT), and the amount of adsorbed hydrogen

Sample	Dispersity Pt_s/Pt_t, %*	Oxygen absorption, (atom O)/(atom Pt_t)		H/Pt_t	H/Pt_s
		OT	OC		
$Pt–Br/Al_2O_3$	91	1.37	0.51	1.72	1.89
$Pt–Cl/Al_2O_3$	100	1.50	0.50	2.0	2.0
$Pt–F/Al_2O_3$	100	1.79	0.60	2.38	2.38
$Pt/SO_4/ZrO_2/Al_2O_3$	16	0.24	0.02	0.44	2.75

* Pt_s and Pt_t are the amount of surface platinum atoms and the total amount of platinum atoms, respectively.

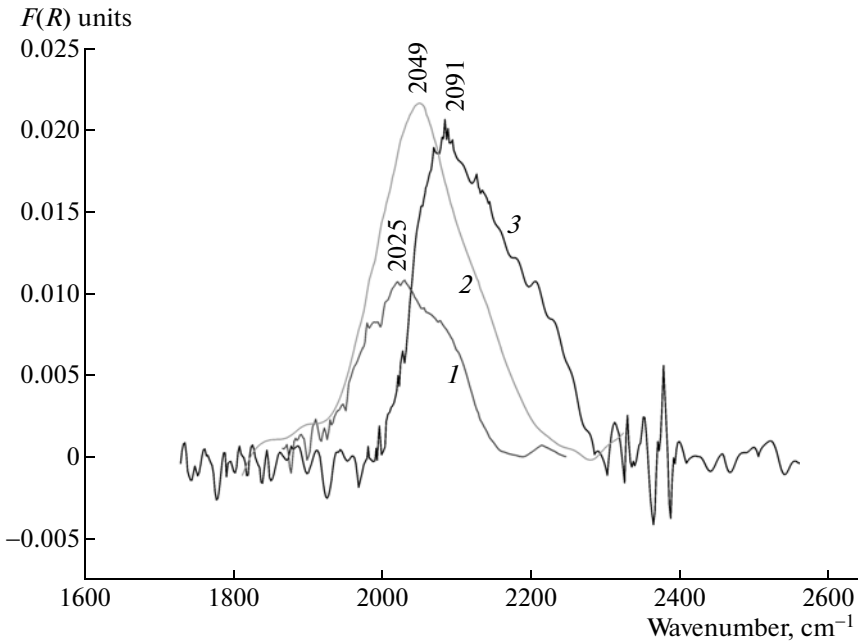

Fig. 5. Diffuse reflectance IR spectra of Pt hydride on (*1*) $Pt–Cl/Al_2O_3$, (*2*) a mixture ($Pt–Cl/Al_2O_3 + SO_4/ZrO_2/Al_2O_3$), and (*3*) $Pt/SO_4/ZrO_2/Al_2O_3$.

acidity halogen, the chemisorption capacity for hydrogen increased to $H/Pt_s = 2.38$. On going to the $Pt/SO_4/ZrO_2/Al_2O_3$ superacid system, a further increase in the amount of adsorbed hydrogen to $H/Pt_s = 2.75$ was observed.

The IR-spectroscopic study of hydrogen adsorption on the surface of platinum-containing catalysts with various states of platinum demonstrated the inhomogeneity of adsorbed hydrogen. Figure 5 shows diffuse reflectance IR spectra in the region of 1700–2600 cm^{-1}. The spectra exhibited absorption bands at 2025, 2049, and 2091 cm^{-1}, which can be attributed to the hydride forms of adsorbed hydrogen. The spectra were recorded after heating and keeping the catalysts in hydrogen at elevated temperatures (300°C for the $Pt–Cl/Al_2O_3$ catalyst and 250°C for the sulfate–zirconia (including mixed) systems). The corresponding absorption bands were not detected without heating in an atmosphere of hydrogen. This fact suggests an activated character of the formation of hydride hydrogen species. In this case, the absorption band frequencies were different to suggest another character of the resulting hydride ions. At the same time, we can note a clearly pronounced tendency: the positions of absorption bands due to hydride ions shifted to a high-frequency region on going to the superacid system.

The formation of hydride ions on platinum upon the adsorption of hydrogen was supported by the H/D exchange. Figure 6 shows the IR spectra obtained upon the $H_2–D_2$ isotope exchange on the surface of $Pt/SO_4/ZrO_2/Al_2O_3$. After a preliminary exposure of the sample in hydrogen at 250°C followed by cooling and evacuation at 20°C, the IR spectrum containing an absorption band at 2089 cm^{-1} was recorded. After the addition of an $H_2–D_2$ isotope mixture (100 Torr) containing 97% D_2 to the measurement cell and a 30-min exposure at room temperature, the next spectrum was recorded, in which the absorption band at 2089 cm^{-1} retained its position and intensity. Noticeable changes in this band were detected after the stepwise heating of the sample to 200°C in steps of 50 K in an atmosphere of the $H_2–D_2$ mixture. The H–D exchange occurred only at a temperature of 100°C: the absorption band at 2089 cm^{-1} shifted toward the region of low frequencies to 1481 cm^{-1}, which corresponds to the Pt–D isotope substitution for Pt–H.

The above experiments demonstrated that hydrogen adsorbed on platinum was inhomogeneous in its composition. The amount of adsorbed hydrogen for the $Pt–X/Al_2O_3$ catalysts corresponded to an atomic ratio of 2 : 1 between hydrogen and platinum, whereas this ratio was about 3 : 1 for the $Pt/SO_4/ZrO_2/Al_2O_3$ superacid system. The found activated adsorption of hydrogen was responsible for the appearance of hydride ions on ionic platinum atoms. It is likely that the proton formed upon the heterolytic dissociation of hydrogen diffused to the support (hydrogen spillover).

Effect of the State of Platinum on Adsorption and Catalytic Properties

The experimental results obtained in this work concerning hydrogen adsorption (Table 4) suggest that the high specific chemisorption of hydrogen in catalysts was related to the presence of ionic platinum. The disperse platinum metal adsorbs hydrogen with the

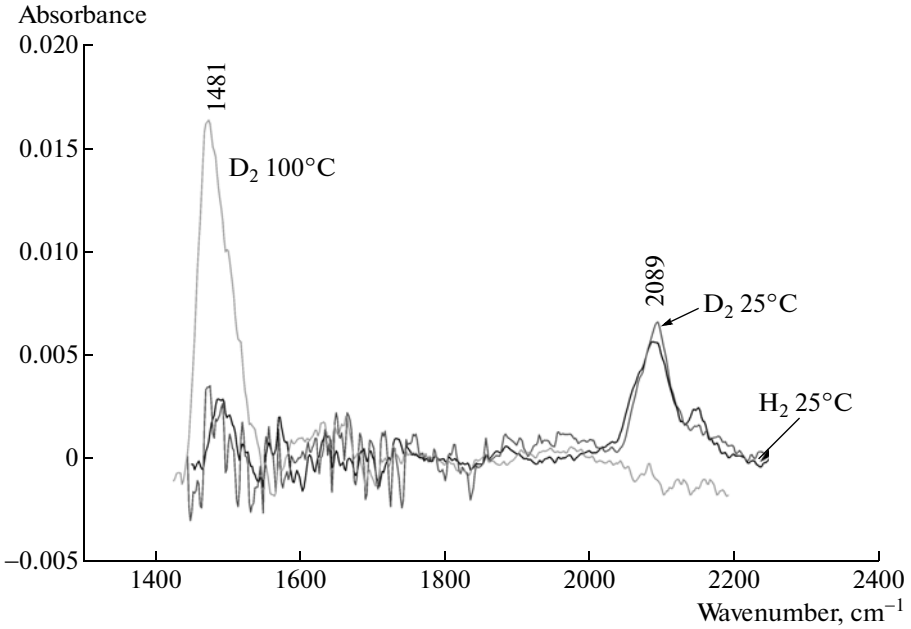

Fig. 6. IR spectra illustrating H/D exchange on $Pt/SO_4/ZrO_2/Al_2O_3$ at 25 and 100°C.

stoichiometry H/Pt = 1, as substantiated in a number of publications [22, 23], whereas the occurrence of ionic platinum in Pt/Al_2O_3 catalysts is currently undoubted [21]. The experimental results suggest that the $Pt/SO_4/ZrO_2/Al_2O_3$ superacid catalyst exhibited the highest capacity of platinum to accumulate hydrogen ($H/Pt_s = 2.75$). Note that the quantitative data on the adsorption of oxygen and hydrogen on this catalyst given in Table 4 can be considered as evidence for special properties of platinum in this system, which are different from the properties of Pt ions in alumina–platinum systems. First, a higher adsorption capacity for hydrogen was observed. Second, a low chemisorption capacity for oxygen ($O/Pt_t = 0.02$) was found, which can be considered as a sign of a higher oxidation state of platinum, as compared with alumina–platinum catalysts.

The high chemisorption capacity for hydrogen ($H/Pt_s = 2.75$) formally allows for the adsorption of hydrogen in both molecular and atomic forms. The molecular adsorption of hydrogen on platinum metal can occur only at low temperatures of about –173°C [27], whereas hydrogen is adsorbed on platinum metal at temperatures higher than 0°C in an atomic form. Therefore, in the isomerization reaction performed on the $Pt/SO_4/ZrO_2/Al_2O_3$ superacid catalyst over the temperature range of 120–220°C under standard conditions, the adsorption of hydrogen should be considered to occur by a dissociative mechanism with the formation of atomic hydrogen on Pt^0 as the constituent of platinum metal particles with a characteristic CO_{ads} absorption frequency of 2099 cm^{-1}. Platinum metal plays an important role in the catalyst. Coke formation is a reason for the deactivation of superacid catalysts; it is responsible for the blocking of strong acid sites by carbon deposits. Allyl and polyenyl cations and polycyclic aromatic compounds, which are formed from alkenes as by-products of the isomerization reaction, act as these compounds [2]. The reaction performed in an atmosphere of hydrogen completely suppressed the formation of compounds of this kind because platinum metal provided the adsorption and supply of atomic hydrogen to acid sites followed by the hydrogenation of polycyclic aromatic compounds formed at the active sites.

According to IR-spectroscopic data, the state of platinum in a superacid catalyst is characterized by the superposition of three characteristic frequencies of 2099, 2116, and 2151 cm^{-1}, which belong to metal atoms (Pt^0), $(Pt–H)^{\delta+}$ structures, and Pt ions in structures like $(SO_3–O)–Pt$, respectively. With the use of H/D isotope exchange, we found that hydride ions were formed upon the adsorption of hydrogen on platinum with an absorption band at 2091 cm^{-1}. The formation of platinum hydrides exhibited an activated character, and it was observed on catalysts containing ionic platinum (Fig. 4). Thus, it is reasonable to relate the appearance of hydride ions to the adsorption of hydrogen on platinum ions. This is also evidenced by the dependence of the absorption frequency of $Pt–H^-$ hydrides on the structure of surface complexes (like $(SO_3–O)–Pt$ or $[PtO_xCl_y]$) containing ionic Pt, which were identified in alumina–platinum and superacid catalysts. It is believed that the adsorption of hydrogen on platinum ions at elevated temperatures occurred by a heterolytic mechanism with the formation of $Pt^+–H^-$ and the proton $O–H^+$ on the support, and the formation of new or the regeneration of spent Brønsted

acid sites (BASs) can occur upon the dissociation of hydrogen on surface platinum complexes. The interaction of acid site protons with metal particles explains the appearance of an absorption band at 2116 cm^{-1} in the IR spectra. This absorption band is ascribed to CO adsorbed on positively charged platinum metal particles, which were formed due to structures like $(Pt^0–H)^{\delta+}$. Theoretical studies with the use of quantum-chemical methods demonstrated that these sites can directly convert alkanes with the formation of metal–carbene intermediates without the direct participation of acid sites [14, 15].

Another consequence of the heterolytic adsorption of hydrogen can be a decrease in the strength of LASs because of the removal and transfer of hydride ions adsorbed at platinum ions and complexes like $(SO_3–O)–Pt$ with a characteristic CO_{ads} frequency of 2151 cm^{-1}. As the strength of LASs decreased as a result of hydride adsorption, the rate of side processes resulting in coke formation also decreased. This facilitated an increase in the selectivity and operational stability of the superacid catalyst. Moreover, ionic platinum can participate as an intermediate in the formation and transfer of hydride ions at the final step of the reaction of hexane isomerization. Shortening the lifetime of reactive intermediates prevents the occurrence of side cracking and polymerization reactions leading to catalyst carbonization.

The specific ability of platinum in the sulfate–zirconia system to activate hydrogen adsorption (in amounts to $H/Pt_s = 2–3$ atom/atom) is responsible for high stability and selectivity characteristics of sulfated zirconium dioxide in the low-temperature region of *n*-hexane isomerization. The dissociative adsorption of hydrogen at platinum ions with the formation of hydride ions and protons facilitates the modification of both types of acid sites (BASs and LASs) to result in the regeneration and formation of new sites and in a change in the acidity of existing hexane isomerization sites in an atmosphere of hydrogen. The ionic form of platinum can act as a source of hydride ions at the final step of the isomerization reaction. On the other hand, the dissociative adsorption of hydrogen on platinum metal is a source of atomic hydrogen for the hydrogenation of coke deposition precursors to provide the stable operation of sulfate–zirconia catalysts.

Ionic platinum as a constituent of the surface sites of the superacid catalyst should be considered as an important reactant in hexane isomerization, which exhibits specific properties by participation in hydrogen activation for hydride transfer or in the modification of surface acid sites of the catalyst. Zero-valent surface platinum atoms are hydrogen activators and suppliers for the hydrogenation of coke deposit precursors, polycyclic aromatic hydrocarbons. Thus, the occurrence of several states of Pt, which are responsible for various functions, provides a high level of activity and operational stability of the catalysts based on sulfated zirconium dioxide for low-temperature isomerization.

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