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Studying the $Pt/SO_4^{2-}/ZrO_2$ Systems Applied onto SiO_2 and Al_2O_3 in the Reaction of *n*-Hexane Isomerization

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Abstract

Zirconium sulphate catalysts applied onto SiO_2 and Al_2O_3 were prepared and investigated. Phase composition inherent in the catalysts, acidic properties according to the adsorption of CO and textural characteristics thereof were investigated. Catalytic activity level in the isomerization reaction of *n*-hexane was determined. It has been demonstrated that the most active catalytic system is presented by a catalyst based on Al_2O_3 carrier. The yield of hexane isomers wit the use of this catalyst amounts up to 75 mass % within the temperature range of 200–220 °C. It has been found that in the case of using alumina as a carrier the catalysts exhibit forming strong acid centers with the absorption bands of adsorbed CO being at 2210 and 2224 cm^{-1}.

Key words: sulphated zirconia, supported catalysts, *n*-hexane isomerization

INTRODUCTION

The isomerization of light gasoline fractions is an important modern refining process resulting in producing high-octane components of motor gasoline containing no aromatic hydrocarbons. This is especially urgent in connection with the introduction of Technical regulation requirements for the quality of motor fuels in Russia [1]. Solving the problem of producing high-octane gasoline with a low content of aromatic hydrocarbons is based on involving isoalkanes in the composition thereof as the products of isobutane alkylation by alkenes and of the isomerization of $C_5–C_6$ alkanes.

In recent years in Russia there was paid great attention to the industrial development of the technology of the isomerization of light gasoline fractions. To date, at the Russian petroleum refineries (PR) there were commissioned and being operated 16 isomerization units with the total capacity with respect to raw material amounting to about 6 million t/year. Constructing and commissioning new installations is being continued [2].

To date, of urgency is search for efficient catalysts for the isomerization of $C_5–C_6$ alkanes. An important place among catalysts the based on chlorinated alumina and zeolites is occupied by the systems involving sulphated zirconia (SZ) [2]. Such catalysts combine a high activity, resistance to poisons, and operation within a favourable range of temperature values (140–220 °C).

One of the ways to increase the activity of catalysts consists in transition from bulk systems to applied ones. Fixing an active ingredient on different porous carriers leads to changing the physicochemical and catalytic properties thereof. So, applying the zirconium sulphate onto SiO_2 and Al_2O_3 carriers causes the increases the SZ specific surface and the number of active centers to increase [3]. Using SiO_2 and Al_2O_3 as substrates causes the tetragonal phase of

ZrO_2 to be stabilized, which phase is active in the isomerization of *n*-alkanes [4]. The interaction between ZrO_2 and the carrier restricts the agglomeration of ZrO_2 particles thereby preventing the transformation of the tetragonal phase to monoclinic one.

The applying influences also upon the acid-base properties of zirconia [5]. The properties of supported SZ systems depend on a method used for the preparation of catalysts [3–11]. As to compare with the bulk systems, supported SZ catalysts were investigated to a lesser extent. To all appearance, this could be connected with the fact that nowadays the supported catalysts are inferior with respect to bulk systems in the level of catalytic activity. The preparation of supported SZ catalysts is connected with choosing a carrier and a precursor of the active component, with impregnation (sorption) conditions and with the process of activation.

The aim of this work consisted in studying the effect of the conditions of preparing the zirconium sulphate catalysts applied from $Zr(SO_4)_2$ precursor onto SiO_2 and Al_2O_3 carriers exerted on the catalytic properties thereof in the reaction of *n*-hexane isomerization.

EXPERIMENTAL

For the preparation of the catalysts, we used silicon oxide and aluminum oxide calcined at 750 °C, as carriers. The fractions of carriers 1–2 mm in particle size were impregnated according to the moisture capacity with an aqueous solution of $Zr(SO_4)_2$ with the zirconium concentration amounting to 169 mg/mL. The solution as prepared *via* dissolving a weighed sample portion of the salt in distilled water, under vigorous stirring and heating for 2 h. The resulting solution was filtered. The content of the active ingredient was varied *via* changing the number of impregnation procedures. The impregnated samples were dried in air and then in an oven at 120 °C. The samples were then calcined in a muffle at 750 °C, or re-impregnated with the solution of $Zr(SO_4)_2$. After the second impregnation, the samples were dried at 120 °C and calcined at 750 °C. The resulting system of SZ/carrier was impregnated with a solution of H_2PtCl_6 according to the moisture capacity with the calculated content of Pt amounting to 0.3 mass %. Thereafter, the samples were dried at 120 °C and calcined then in flowing dry air at 450 °C.

Determining the content of Pt, ZrO_2 and SO_4^{2-} ions in the samples under investigation was performed by means of a Varian 710ES atomic emission spectrometry with inductively coupled plasma under the following conditions: plasma power 1.1 kW, plasma-forming argon flow 13.5 L/min, auxiliary argon flow 1.5 L/min, analytical wavelengths 343.823 (Zr), 214.424 (Pt) and 181.972 nm (S). For the decomposition of the samples, the weighed portions of the samples were placed in glassy carbon beakers, added 10 mL of HF (conc.) and 2 mL of $HClO_4$ (70 %) heated until perchloric acid vapours ceased to evolve. To a dry solid residue was added 10 mL HCl (1 : 1) and heated the mixture to dissolve the salts formed. The resulting solutions were transferred to volumetric flasks with adding bidistilled water up to the target mark.

The parameters of the porous structure obtained were investigated using a Sorptomatic-1900 unit. When calculating the specific surface area it was taken into account that the molecular nitrogen in the "landing field" in the completed monolayer amounts to 0.162 nm^2. The total or adsorption pore volume was determined from the adsorption level of nitrogen at 77 K and $P/P_s = 0.996$. The molar volume of liquid nitrogen at the temperature of experiment was taken to be 34.68 cm^3/mol.

The XRD studies were performed with the use a D8 Advance diffractometer (Bruker) in a parallel CuK_α radiation within an angular range $2\theta = 5–80$ deg. The scanning pitch was equal to 0.05 deg, the signal integration time amounting to 5 s per pitch.

The IR spectra of the samples were registered using a Shimadzu FT-8300 spectrometer with the resolution of 4 cm^{-1} and the spectra accumulation number equal to 100. For the registration of the spectra the samples were pressed into tablets with no binder, to a density of $24 \cdot 10^{-3}$ g/cm^2. A tablet was placed in a cuvette with further performing the sample pretreatment at an elevated temperature, the adsorption of CO to register the spectrum at

TABLE 1

Chemical composition of catalysts under investigation

Samples	Carriers	Number of impregnation procedures	Mass fraction, %			
			ZrO_2	SO_4^{2-}	SO_4^{2-}/ZrO_2	Pt
$Pt/SZ/SiO_2$-1	SiO_2	1	36	3.1	1 : 10	0.3
$Pt/SZ/SiO_2$-2	SiO_2	2	46	4.1	1 : 10	0.3
$Pt/SZ/Al_2O_3$-1	Al_2O_3	1	17	6.7	2 : 5	0.3
$Pt/SZ/Al_2O_3$-2	Al_2O_3	2	26	12	1 : 2	0.3

liquid nitrogen temperature (−190 °C). Before the adsorption, the sample was heated under vacuum at 500 °C for 1 h. The adsorption of CO was performed within the pressure range of 0.1−10 Torr.

The catalytic investigations were carried out using a flow-through unit, with an isothermal tubular reactor with a fixed catalyst bed and a thermocouple pocket located along the axis of the reactor. The reactor was loaded with 2 cm^3 of a catalyst (fraction 0.25−0.75 mm). The activation of supported catalysts was carried out directly in the catalytic unit with a purified hydrogen flow during 2 h at 270 °C. The catalytic reaction was carried out within the temperature range of 140−260 °C at a pressure of 1.5 MPa, the flow rate of feeding the liquid being of 0.5 h^{-1}, the molar ratio $H_2/n\text{-}C_6 = 3 : 1$. The raw material was presented by kh. ch. (chemical purity) grade *n*-hexane that was preliminary dried using NaX molecular sieve, with further feeding by a dosing pump to a tee for mixing with hydrogen and then into the reactor. The reaction products were analyzed in an on-line mode using a Tsvet-800 chromatograph with a Petrocol DH 50.2 capillary column.

RESULTS AND DISCUSSION

Chemical composition

In order to prepare the samples on SiO_2 as a carrier, we have chosen silica gel with developed porous structure ($S_{sp} = 308$ m^2/g, $V_{por} = 0.94$ cm^3/g). For the preparation of samples on Al_2O_3 we used a commercial A-64 grade of γ-Al_2O_3 ($S_{sp} = 154$ m^2/g, $V_{por} = 0.65$ cm^3/g). Prior to applying the original carrier was calcined at 750 °C and further wetted with a solution of $Zr(SO_4)_2$ according to moisture capacity. The resultant carrier was dried and calcined at 750 °C, and then platinum was applied with further calcining the catalyst in a flow of dry air.

The results of the chemical analysis of componential content in the catalysts are presented in Table 1. In the case of SiO_2 after the first impregnation, the ZrO_2 content up to 36 mass %, whereas in the case of Al_2O_3 this value amounts to 17 mass %, which is connected with the difference in the pore volume of carriers. After the second impregnation the content of the active component increases, the content of ZrO_2 is equal to 46 mass % for SiO_2 and 26 mass % for Al_2O_3.

Alongside with the real content of sulphate groups and ZrO_2, the catalytic activity is also influenced by the ratio between the two components [12]. Table 1 demonstrates calculated mass ratio values for the starting compounds and the catalysts prepared. It can be seen that the samples applied onto SiO_2 and Al_2O_3 differ in this parameter to a considerable extent. So, the samples based on SiO_2 with a single and double impregnation the ratio SO_4^{2-}/ZrO_2 is the same amounting to 1 : 10, *i. e.* the most part of the sulphate groups is removed in the course of calcination. For a sample based on Al_2O_3 after single impregnation the ratio is equal to 2 : 5, and after the re-treatment by $Zr(SO_4)_2$ this value increases up to 1 : 2. Thus, in the case of applying onto Al_2O_3 the zirconium sulphate (the active component precursor) is stronger fixed on the substrate.

Textural properties

Table 2 demonstrates the parameters of the porous structure of the original carriers and

TABLE 2

Textural characteristics of the original carriers and the catalysts obtained

Samples	S_{sp}, m^2/g	V_{por}, cm^3/g	D_{ef}, Å
SiO_2	308	0.94	120
Pt/SZ/SiO_2-1	172	0.40	98
Pt/SZ/SiO_2-2	147	0.36	97
Al_2O_3	154	0.65	169
Pt/SZ/Al_2O_3-1	114	0.36	127
Pt/SZ/Al_2O_3-2	59	0.15	100

Note. D_{ef} is effective pore diameter.

of the catalysts obtained. It can be seen that the single impregnation of carriers with saturated $Zr(SO_4)_2$ solution leads to filling the pore space of the carriers, which is indicated by decreasing the specific surface and pore volume. The repeated impregnation of the catalyst based on SiO_2 causes reducing the specific surface area from 172 to 147 m^2/g and the pore volume from 0.4 to 0.36 m^3/g. The repeated impregnation of Al_2O_3 leads to significantly changing the textural characteristics: the specific surface area and pore volume exhibit an almost two-fold decrease.

Figure1 presents the plots of pore size distribution calculated from the desorption isotherm branches. It is seen that in the case of catalysts applied onto SiO_2, a polymodal character of pore size distribution is conserved, whereas the average pore size is shifted toward low mesopore size ranging within 40–60 Å. Catalysts applied onto Al_2O_3, exhibit a more complicated picture: after single impregnation the monomodal character of pore size distribution is conserved, whereas the effective pore diameter remains almost unchanged. For the re-impregnated samples, the main peak is shifted to small mesopores with the size of about 70 Å. Simultaneously, the distribution curve exhibits false peaks at 37–39 Å, inherent only in lay-

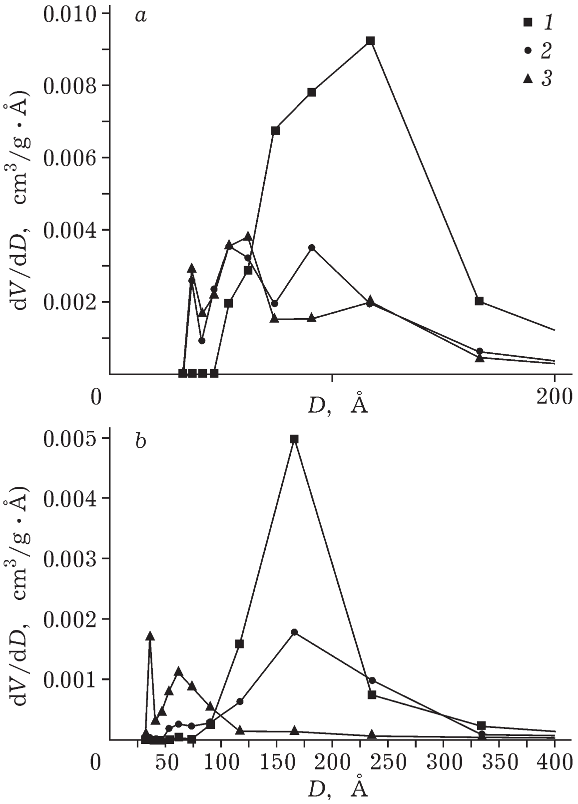

Fig. 1. Pore size distribution for SiO_2 and Al_2O_3 and for catalysts with a single- and double impregnation of SiO_2 (*a*) and Al_2O_3 (*b*): *1* – carrier, *2* – single impregnation, *3* – double impregnation.

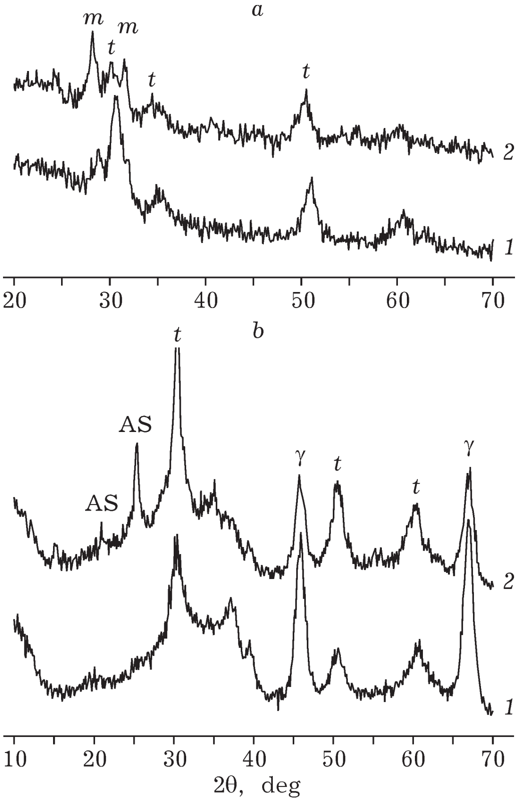

Fig. 2. XRD patterns for samples applied SiO_2 (*a*) and Al_2O_3 (*b*) calcined at 750 °C: *1*, *2* – one and two impregnation procedures, respectively; *t* and *m* are tetragonal and monoclinic phase of ZrO_2 respectively; γ – γ-Al_2O_3, AS – $Al_2(SO_4)_3$.

TABLE 3

Data on the concentration of adsorbed CO on the LAC, μmol/g

Samples	LAC-1	LAC-2	LAC-3	LAC-4
Pt/SZ/SiO_2-1	120 (2189)	79 (2199)	7 (2209)	–
Pt/SZ/Al_2O_3-1	117 (2187)	107 (2199)	31 (2210)	2.4 (2224)
Pt/SZ/Al_2O_3-2	81 (2187)	91 (2199)	45 (2210)	5.8 (2224)

Note. In parentheses, the position of the bands is presented (in cm^{-1}).

ered systems and connected with the calculation method [13]. In this case, this could be caused by a layered nature of the structure formed by fixing the active $Zr(SO_4)_2$ phase in the course of repeated impregnation.

Phase composition

The results of the XRD analysis of the catalysts prepared are presented in Fig. 2. The XRD patterns of the samples based on SiO_2 (see Fig. 2, *a*), exhibit the peaks inherent in the crystalline phases of zirconia such as the monoclinic phase (m-ZrO_2) and the tetragonal phase (t-ZrO_2). The catalyst prepared via a single impregnation of SiO_2 exhibits the peak intensity t-ZrO_2 to exceed the peak intensity of m-ZrO_2, which could indicate the predominance of the tetragonal phase in the mentioned sample. Dispersing the $Zr(SO_4)_2$ over the carrier surface leads to the formation of fine primary ZrO_2 particles, which promotes the stabilization of the metastable tetragonal phase of ZrO_2 [14]. The sample with double impregnation exhibits prevailing the m-ZrO_2 phase. To all appearance, increasing the SZ amount after the second impregnation procedure results in enlarging the size of the primary particles, which eventually promotes the formation of the monoclinic ZrO_2 phase [14].

The XRD pattern of the sample based on Al_2O_3 (see Fig. 2, *b*) after single impregnation exhibits the peaks inherent in t-ZrO_2 and γ-Al_2O_3. The broadening of the peak within the range of angles $2\theta = 27-34$ deg corresponding to t-ZrO_2 indicates a part of ZrO_2 to be in the amorphous state. The sample with double impregnation exhibits increasing the crystallinity level of t-ZrO_2, whereas the intensity of the peaks corresponding to γ-Al_2O_3 decreases with appearing the reflexes corresponding to the phase of aluminum sulphate. Basing on these data it can be concluded that with repeated processing the sample by the solution of $Zr(SO_4)_2$ applied onto Al_2O_3, there occurs a deep interaction between the precursor of the active component with the carrier, whereby the phase of $Al_2(SO_4)_3$ is formed.

Acidic properties

The acidic properties of the catalysts can be judged basin on the number of Lewis acid centers (LAC) (Table 3). The concentration of LAC was measured taking into account the integral band intensity considering of the adsorbed CO (within the spectral region of 2185–2240 cm^{-1}) according to formula: N [μmol/g] = A/A_0, where A is the integrated intensity of the band inherent in adsorbed CO; A_0 is the integrated absorption coefficient, taken from [15]. The strength of the acid centers exhibits an increase with increasing the vibration frequency of adsorbed CO [15].

The comparative analysis of the acidic properties of the samples applied onto SiO_2 and Al_2O_3 (Table 3) demonstrates that the weak-acid centers (LAC-1) and medium-acid ones (LAC-2) inherent in SZ, are prevailing in the case of SiO_2 supported catalysts. The Al_2O_3 supported samples exhibit the fraction of these centers to decrease, whereas there occurs increasing the fraction of the strongest Lewis acid centers LAC-3 therein. In the case of a repeated impregnation of samples based on Al_2O_3 the number of LAC-1 and LAC-2 centers decreases, whereas the fraction of strong-acid centers LAC-3 and LAC-4 increases. To all appearance, this could be connected with a higher SO_4^{2-}/ZrO_2 ratio, and with the formation of aluminum sulphate phase.

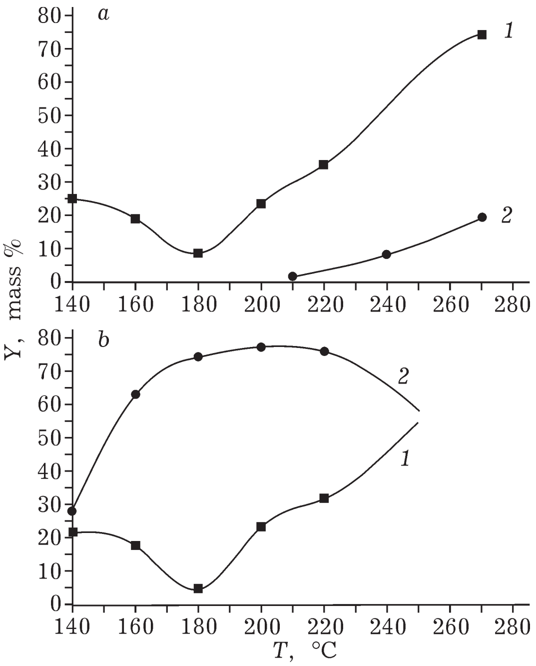

Fig. 3. Total yield of hexane isomers (*Y*) on catalysts applied onto SiO_2 (*a*) and Al_2O_3 (*b*): *1*, *2* – one and two impregnation procedures, respectively.

Thus, the use of Al_2O_3 as a carrier allows one to obtain catalysts with an increased content of strong LAC.

Isomerization of n-hexane

Figure 3 demonstrates the conversion of *n*-hexane on SZ catalysts, applied onto SiO_2 and Al_2O_3. It is seen that in the case of the sample with a single impregnation of SiO_2 (see Fig. 3, *a*) one can consider the two areas of activity. Within the temperature range from 140 to 180 °C there occurs decreasing the total yield of hexane isomers. To all appearance, the decrease of the activity could be connected with blocking the active centers of the catalyst *via* the formation of coke precursors [12]. With increasing the temperature, the active centers are regenerated *via* the hydrogenation of coke precursors resulting in the catalyst recovery and growing the activity thereof. The yield of hexane isomers increases with increasing the temperature up to 270 °C. This temperature is chosen as the limiting temperature of conducting the experiments, since at 280–300 °C there occurs a noticeable degradation of the active surface (acidic centers) due to the reduction of SO_4^{2-} ions [16].

The sample with a double impregnation of SiO_2 demonstrates very low yields of hexane isomers up to the temperature of 270 °C, which could be caused by a reduced content of the tetragonal phase *t*-ZrO_2 and by prevailing the *m*-ZrO_2 phase (see Fig. 2). To all appearance, this could be connected with an increase in average particle size with increasing the SZ mass fraction in the sample [17].

Figure 3, *b* presents the curves plotted for the yield of hexane isomers using the samples based on Al_2O_3. It can be seen that the yield curve for the sample with a single impregnation of Al_2O_3 is similar to the curve obtained for catalyst the based on SiO_2. At low temperature values (140–180 °C), the catalytic activity decreases due to the formation of coke deposits that block the active centers. When the temperature rises over 200 °C the activity is restored due to the hydrogenation of coke precursors.

The repeated impregnation of alumina causes significantly changing the catalytic activity of the sample. The yield of hexane isomers using the sample after the second impregnation increases continuously up to 220 °C to reach 75 mass % within the temperature range of 200–220 °C. To all appearance, the increased activity is associated with prevailing the most strong acidic centers, characterized by the adsorption of CO corresponding to absorption peaks at 2210 and 2224 cm^{-1}. The formation of these types of acidic centers, to all appearance, could be connected with a higher content of SO_4^{2-} in the sample with double impregnation.

CONCLUSION

Using the method of $Zr(SO_4)_2$ thermolysis in the pores of SiO_2 and Al_2O_3 carriers there were catalysts synthesized active in *n*-hexane isomerization reaction. The most active catalysts were prepared basing on alumina carrier. Considerable increasing the catalyst activity occurs in the case of a catalyst obtained via double impregnation of Al_2O_3. This sample demonstrates the highest concentration of sulphate ions as well as the highest SO_4^{2-}/ZrO_2 ratio. Furthermore, there is mainly tetragonal phase *t*-ZrO_2 formed therein, which promotes the formation of strong

LAC with the absorption peak at 2210 cm^{-1}, and strong LAC with the absorption peak at 2224 cm^{-1}, inherent in the formation of aluminum sulphate. As the result, the catalytic activity of these systems in the isomerization reaction of *n*-hexane exhibits an increase.

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