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Aluminum oxide carrier for a catalyst for low-temperature isomerization of hydrocarbons

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Objectives. *Determine the necessary conditions for obtaining a granulated η-Al_2O_3 carrier, investigate its structural and strength properties, and evaluate its activity for the model n-butane isomerization reaction.*
Methods. *Samples containing bayerite structure aluminum trihydroxide were synthesized by precipitation from aqueous solutions of aluminum nitrate with ammonia under isothermal conditions at a constant pH value. The samples of the granulated carrier were obtained using an extrusion method when the composition of molding pastes was varied by tuning the ratio of bayerite- and η-Al_2O_3-containing components and introducing polyvinyl alcohol.*
Results. *The influence of the preparation conditions on the structural and strength properties of the active Al_2O_3 granules is evaluated. Samples of the aluminum oxide carrier were tested for a model reaction of low-temperature isomerization of n-butane, demonstrating a sufficiently high selectivity and reasonable prospects for use as catalysts for low-temperature isomerization of hydrocarbons.*
Conclusions. *Increasing the content of the polyvinyl alcohol in the molding paste from 0.4 to 1.8 wt % is accompanied by an increase in the predominant sizes of the mesopores in the range of 10–50 nm and pores in the range of 50–80 nm, explaining the high values of all recorded parameters for the process of isomerization of n-butane.*

Keywords: *isomerization, n-alkanes, the carrier of the catalyst for isomerization, aluminum oxide, bayerite.*

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Алюмооксидный носитель для катализатора низкотемпературной изомеризации углеводородов

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Цели. *Определение условий получения гранулированного η-Al_2O_3-носителя, исследование его структурно-прочностных свойств и оценка активности в модельном процессе изомеризации н-бутана.*

Методы. *Образцы, содержащие тригидроксид алюминия байеритной структуры, синтезированы осаждением из водных растворов нитрата алюминия аммиаком в изотермических условиях при постоянном значении pH. Экструзионным методом получены образцы гранулированного носителя при варьировании состава формовочных паст: соотношения количеств байерит- и η-Al_2O_3-содержащих компонентов и введения поливинилового спирта.*

Результаты. *Оценено влияние условий приготовления на структурно-прочностные свойства гранул активного Al_2O_3. Образцы алюмооксидного носителя испытаны в модельной реакции низкотемпературной изомеризации н-бутана, показана их достаточно высокая селективность и перспективность при получении катализаторов низкотемпературной изомеризации углеводородов.*

Выводы. *Увеличение содержания поливинилового спирта в формовочной пасте от 0.4 до 1.8 масс. % сопровождается смещением преобладающих размеров мезопор в интервале 10–50 нм и пор в интервале 50–80 нм в большую сторону, что объясняет высокие значения всех регистрируемых показателей процесса изомеризации н-бутана.*

Ключевые слова: *изомеризация, н-алканы, носитель катализатора изомеризации, оксид алюминия, байерит.*

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INTRODUCTION

The process of isomerization of linear alkanes to produce automobile fuels is a key stage for ensuring the conversion of low-octane unbranched paraffins to high-octane branched molecules. This process can be considered an effective and economically viable way to increase the octane number of motor gasoline without forming significant quantities of aromatic compounds [1].

The isomerization process occurs on acid catalysts and can be initiated by strong Lewis acids, Friedel–Crafts catalysts, at relatively low temperatures but with the significant disadvantages of instability and highly corrosive nature [2, 3]. In industrial isomerization processes, solid acids with platinum deposits are usually used as catalysts, of which platinum deposited on chlorinated aluminum oxide or zeolites are the most commonly used catalytic systems [4–6]. Zeolites are less acidic than chlorinated aluminum oxides, thus requiring higher temperatures (250–400°C) for isomerization to occur, resulting in the lower production of branched isomers [3, 7].

The most active catalysts currently used for the isomerization process are chlorinated aluminum-platinum catalysts (Pt/Al_2O_3-Cl). The increased activity of these catalysts allows isomerization at low temperatures of 120–180°C, with high degrees of conversion (X = 28%) and selectivity (S = 98%) for the target product [7, 8].

Aluminum oxide is widely used as a carrier for aluminum-platinum catalysts, in particular the γ- and η-Al_2O_3 forms. However, the η-Al_2O_3 oxide demonstrates advantages over γ-Al_2O_3 in some cases, as granulated η-Al_2O_3 is characterized by both a high specific surface area (S_{sp} = 300–400 m^2/g) and the presence of large mesopores with a size of more than 25 nm ($V_{mesopores}$ = 0.10–0.25 cm^3/g), as well as increased Lewis acidity [2].

η-Al_2O_3 oxide is primarily obtained by the heat treatment of bayerite structure aluminum trihydroxide. The most common method for obtaining bayerite is via precipitation from aqueous solutions of aluminum salts with solutions of ammonia or alkalis [9]. The precipitation of aluminum hydroxide is generally conducted at pH values of 10–11, at which bayerite falls out as large, poorly hydrated, and loosely packed crystals with gaps filled with colloid-bound water. However, the link of water in bayerite, unlike pseudoboehmite, is not durable. Therefore, bayerite precipitates are considerably more thixotropic and under the influence of the shear loads that occur during the preparation of the molding pastes and their extrusion, sharply liquefy. When the shear loads are reduced, they become sharply structured, significantly complicating the process of forming the trihydroxide [10]. Researchers found that this property occurs in a much greater extent in molding pastes made of bayerite precipitated from aluminum salts by ammonia, compared to those obtained using sodium hydroxide as the precipitator [11]. In the latter case, careful washing of the precipitate is required, as strict restrictions exist on the levels of sodium (no more than 0.02 wt %) in carriers for isomerization catalysts [11]. This leads to prioritizing precipitating bayerite with ammonia, as the high structuring of the pastes obtained from hydroxide complicates their extrusion and requires finding conditions for the preparation of granulated oxide η-Al_2O_3 that meet the suitability requirements for a hydrocarbon isomerization catalyst.

A promising method of regulating the properties of aluminum oxide-based molding pastes is changing the properties of the dispersed phase by introducing aluminum oxide powder as a heterogeneous additive [12] and the dispersion medium by introducing a water-soluble organic polymer, polyvinyl alcohol (PVA), as a surfactant. The content of the dispersed phase plays an important role in the system [13].

The objective of this work was to determine conditions for obtaining a granular η-Al_2O_3 carrier, study its structural and strength properties, and evaluate its activity for *n*-butane isomerization.

MATERIALS AND METHODS

Obtaining experimental bayerite-containing samples by deposition

Samples containing bayerite structure aluminum trihydroxide were obtained by precipitation of an aluminum salt solution with an ammonia solution. Nonahydrate aluminum nitrate $Al(NO_3)_3{\cdot}9H_2O$ (GOST 3757-75, batch 25, *NevaReaktiv*, Russia, purity 97%) was used as the initial reagent for preparing a 5 mol/L salt solution. A 25% solution of ammonia $NH_3{\cdot}H_2O$ (GOST 3760-79, batch 49, *NevaReaktiv*, Russia, purity 25%) was diluted to give a 5 mol/L ammonia solution. The following conditions for the preparation of bayerite-containing samples were based on prior literature results [14].

The solutions were mixed in a glass reactor containing an ammonia buffer solution of pH = 10.3–10.5 with constant stirring (the speed of rotation of the agitator is ~300 rpm). Simultaneous supply of the solutions of aluminum nitrate and ammonia to the reactor was performed using a peristaltic pump with a flow rate of 1 and 5 mL/min, respectively. The reaction medium was maintained at a constant pH value of 10.5 ± 0.1, which was monitored at 30 min intervals. The set pH value was created by a 5-fold excess of ammonia relative to the stoichiometry of the reaction:

$$Al(NO_3)_3 + 3NH_4OH = Al(OH)_3\downarrow + 3NH_4NO_3$$

Using a thermostat, the temperature of the reaction medium was maintained at 20 ± 1°C. Under isothermal conditions, the duration of the deposition process was 2 h, and the duration of the aging process of the resulting sediment was 24 h.

The resulting precipitate was separated using a Buchner funnel and washed a neutral reaction pH. The precipitate was dried at a temperature of 100–110°C to a constant mass. The content of bayerite in the synthesized hydroxide precipitate was 85 ± 2 wt % [14].

Obtaining systems containing η-Al_2O_3

During this work, a series of carriers were obtained by the extrusion method (Table 1), differing in their ratios of the amounts of introduced bayerite- and η-Al_2O_3-containing components.

For the production of carrier granules, molding pastes were prepared using powdered components: bayerite-containing hydroxide (hereinafter bayerite), dried at 110°C and η-Al_2O_3-containing aluminum oxide (hereinafter η-Al_2O_3), obtained by the calcination of synthesized hydroxide at 500°C.

When mixed with distilled water, bayerite powder or its mixtures with 20–80 wt % oxide powder undergo further homogenization with the application of shear loads. However, pastes suitable for extrusion could not be obtained.

Using a five percent polyvinyl alcohol/distilled water solution as a plasticizer allowed the homogenized pastes to be formed in a screw granulator through a 2-mm-diameter die.

Extrudates, after “drying” at 20 ± 2°C for 16–18 h and drying at 100–110°C to constant mass, were heat-treated at 280–290°C and 500–510°C for 4 h at each temperature (temperature rise rate of 10°C/min).

Table 1. Compositions of molding pastes

Sample No.	Bayerite	η-Al_2O_3	Humidity,* wt %	PVA**, wt % (in relation to bayerite)
	wt % (according to Al_2O_3)			
1	20	80	49.5	2.7
2	40	60	51	
3	60	40	52	
4	80	20	55	
5	100	0	56	

*ratio of the total mass of water contained in each component to the total mass of all components;
**PVA—polyvinyl alcohol.

Sample characterization methods

Differential thermal (DTA) and thermogravimetric analysis of synthesized bayerite samples were performed in an air atmosphere on a SHIMADZU DTG-60H derivatograph at a heating rate of 10°C/min from room temperature to 800°C. The mass of per sample was ≈ 15–50 mg. The temperature was determined with an accuracy of 1°C and the mass change with an accuracy up to 0.1%. Quantitatively, the phase composition of the samples was determined based on the observed mass loss as a result of thermolysis. The phase composition of the dried bayerite samples was studied by X-ray phase analysis, using a multifunctional X-ray diffractometer "RigakuSmartLab 3" (*RigakuCorporation*, Tokyo, Japan) with CuKα-monochromatic radiation in the range of angles $2\Theta = 10°–80°$ with a scanning speed of 10 °C/min. The volume of the loaded sample was no less than 0.1 cm^3, and the angular resolution of the reflections was up to 0.01°. Transcription of the radiographs was performed using Crystallographica Search-Match V. 2,0,3,1 Oxford Cryosystems, and the standard database was used for decryption.

The fractional composition of powders of the synthesized samples of bayerite and η-Al_2O_3 used for the preparation of molding pastes was determined by laser scattering using the SALD-2201 Laser Diffraction Particle Size Analyzer (*SHIMADZU*, Japan).

The surface acidity function (H_0) of the carrier samples was determined by pH-metry, using a pH meter-millivoltmeter pH-673.M with a glass electrode EVL-1M3 in an aqueous medium exhibiting pH_{H2O} in the range 6.4–6.6, according literature methods [15].

The specific surface area (S_{sp}) of granulated experimental samples was determined by the thermal desorption of nitrogen, using the single-point Bruner-Emmet-Teller method.

Tests of granulated sample strength during crushing "on the end" ($P_{\square}$) were conducted using a MP-2C extensometer device according to prior literature [17].

The determination of the total pore volume (V_Σ) of granular samples by moisture capacity was performed, using water as a pycnometric liquid [18].

Studies of the distribution of pore volume by size were carried out using nitrogen porometry. Nitrogen adsorption/desorption isotherms were determined using a "Autosorb 6iSA" facility (*Quantachrome Instruments*, USA) after degassing the samples in a vacuum oven at 250℃ for 1 h. The specific surface area, specific pore volume (pore filling with adsorbate at its relative pressure ≈ 1), and average effective pore size were determined using density functional theory [16].

To determine the relative activity of carrier samples to evaluate their prospects as effective acid isomerization catalysts, tests were performed for the *n*-butane isomerization reaction, using the method of *NPF OLKAT* company in accordance with established recommendations [19]. The tests were performed while loading the catalyst carrier, 3.0 cm^3, under the following conditions: reactor inlet temperature was 75°C, the volume flow rate of *n*-butane (per liquid) was 1 h^{-1}, and the molar ratio of H_2 : *n*-butane was maintained at 1 : 1. Analysis for the content of isomerizate in the gas mixture at the reactor exit was performed by gas chromatography [19].

The research was carried out on research equipment provided by the Engineering Center of the Saint-Petersburg State Technological Institute (Technical University) and *NPF OLKAT*.

RESULTS AND DISCUSSION

Figure 1 presents the results of the phase composition study on the synthesized samples of aluminum hydroxide by X-ray phase analysis. The diffraction maxima, which are characteristic for aluminum hydroxides of bayerite and boehmite structures, are determined based on the given X-ray pattern.

The study of the aluminum hydroxide samples by DTA allowed us to quantify the content of bayerite structure aluminum trihydroxide in the samples. According to calculations based on mass loss, deposition under experimental conditions (for 2 h of deposition and 24 h of aging) leads to the formation of 85 ± 2 wt % bayerite. Figure 2 shows the derivatogram of the resulting sediments.

When heated, two endoeffects can be observed on the DTA curve with minimums at 63°C and 278°C. The first is related to the removal of physically adsorbed water. Literature data [9, 10, 20] show that the phase transition of bayerite to η-Al_2O_3 occurs in the temperature range of 250–350°C, the cause of the second endothermic effect.

The quantitative evaluation of the phase composition of the calcination product of the synthesized bayerite powder at 500°C shows a content of 80 wt % η-Al_2O_3 and 20 wt % γ-Al_2O_3 [14].

The fractional compositions of the powders of the synthesized sample of bayerite and η-Al_2O_3 used for the preparation of molding pastes are shown in Fig. 3, 4 and in Table 2.

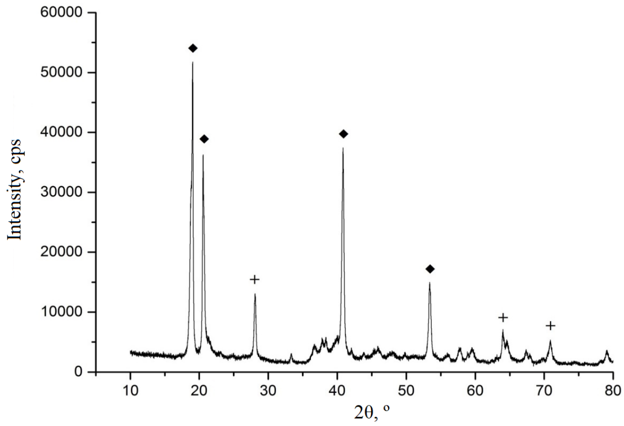

Fig. 1. X-ray diffraction pattern of the synthesized bayerite sample (♦ – bayerite; + – boehmite).

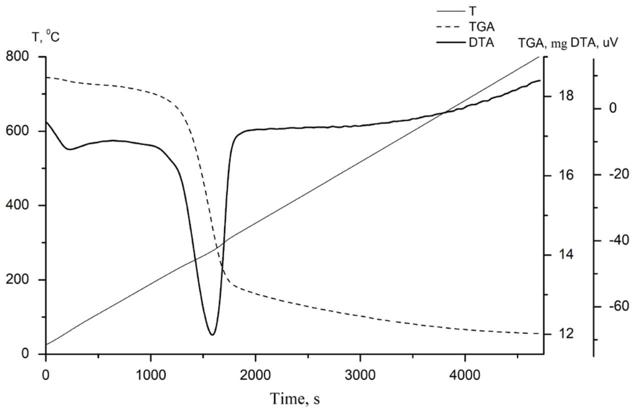

Fig. 2. Derivatogram of a synthesized bayerite sample.

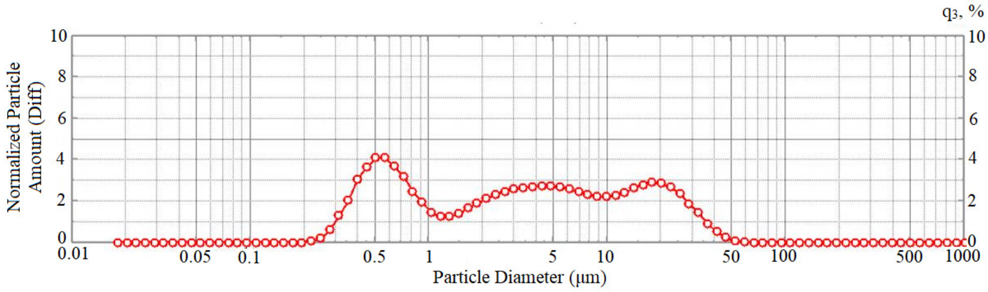

Fig. 3. Differential particle size distribution curve of bayerite powder.

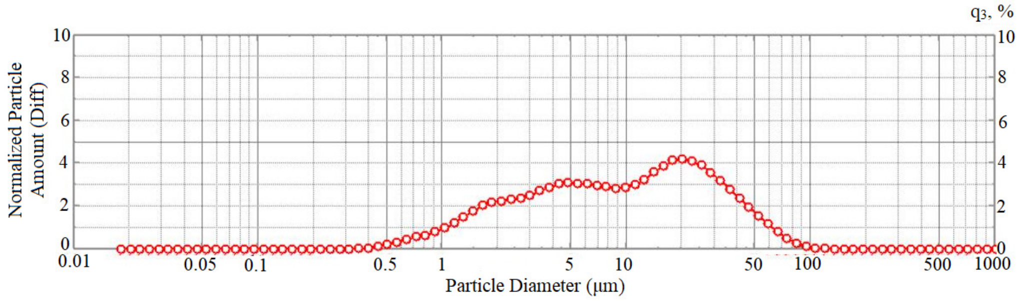

Fig. 4. Differential particle size distribution curve of η-Al_2O_3 powder.

Table 2. Fractional composition of bayerite and η-Al_2O_3 powders used for the preparation of molding pastes

Sample	Fraction, µm	Content, wt %	Prevailing size,* µm
Bayerite	0.2–1	30.6	0.5
	1–10	42.0	5
	10–50	27.4	19
η-Al_2O_3	0.5–3	21.5	2
	3–10	30.4	5
	10–100	48.1	20

*equivalent diameter

Based on the obtained results, a bayerite precipitate with particles ranging in size from 0.2 to 50 µm is formed during deposition under the experimental conditions with particles of around 1 to 10 µm (42 wt %) predominating. Heat treatment of this sample at 500°C to produce η-Al_2O_3 leads to an increase in the particle size to 100 µm. At the same time, a decrease in the number of particles of the 0.5–3-µm fraction occurs.

The results of measurements of the surface acidity function, specific surface area, porous structure parameters, the crushing strength of granules, as well as the total pore volume of granular carrier samples are presented in Table 3.

The determination of the acid-base properties of the various carriers indicates that the studied conditions of their preparation do not affect the value of the Gammet function, $H_0 = 7.1 \pm 0.1$.

An increase in the proportion of bayerite powder in the molding paste (from sample 1 to sample 5) corresponds to an increase in the values of the following textural characteristics of the carrier granules: S_{sp} from 285 to 365 m^2/g, V_Σ from 0.68 to 0.76 cm^3/g, and $P_{\square}$ from 0.6 to 2.0 MPa.

These trends can be explained by the cumulative effect of changes that occur when particles are packed in pastes or granules, as well as the formation of interparticle contacts that ensure the strength of the porous body on the secondary porous structure and strength of granules. First, from sample 1 to sample 5, the proportion of smaller particles increases, increasing the number of single contacts per unit contact section and the proportion of reactive particles (hydroxide compared to oxide). Thus, the number of higher strength contacts increases, contributing to an increase in strength and a decrease in pore size. Second, an increase in the content of a burnout additive-PVA leads to the formation of an additional volume of secondary pores, increasing the total volume of pores V_Σ and decreasing the overall strength.

Data on the distribution of pore volume based on size, calculated from the integral and differential curves obtained from the results of the azotoporometry, are shown in Table 4.

According to the results shown in Table 4, an increase in the share of bayerite in the molding paste leads to a shift in the prevailing d_{max} pore size in the range of 3–10 nm from 4.6 to 3.7 nm and an increase in their volume from 0.12 to 0.14 cm^3/g. The change in these parameters is accompanied by an increase in the pore surface area in the range of 3–10 nm, as well as the "total" S_{sp} of carrier samples (see Tables 3 and 5). At the same time, (Table 4) a slight increase occurs in the prevailing pore sizes and volumes of larger pores, producing mesopores in the range of 10–50 nm (d_{max} from 27.4 to 31.5 nm and $V_{pores\ (10–50)}$ from 0.16 to 0.24 cm^3/g) and pores in the range of 50–80 nm (d_{max} from 65.2 to 77.8 nm and $V_{pores\ (50–80)}$ from 0.08 to 0.16 cm^3/g). This reflects changes in the secondary porous structure of the granules and may be due to the influence of the burning additive-PVA (see Tables 3 and 5).

The nitrogen adsorption-desorption isotherms of the synthesized carriers are shown in Fig. 5.

The sorption isotherms of all carrier samples, with some quantitative differences in the adsorption values at certain relative pressure values P/P_0, where P and P_0 are the equilibrium pressure and the saturated vapor pressure of the adsorbate at the adsorption temperature, respectively, exhibit the same shape. Hysteresis of all samples is H3 type, usually characterized by slit-like pores with almost flat-parallel walls. The adsorption branches of these isotherms exhibit the form typical of type II from the Brunauer classification, indicating the presence of polymolecular adsorption. No horizontal

Table 3. Properties of carrier samples

Characteristics	Sample No.				
	1	2	3	4	5
Surface acidity function H_0	7.1	7.1	7.1	7.0	7.2
Specific surface S_{sp}, m^2/g	285	290	300	310	365
Total pore volume V_{Σ}, cm^3/g	0.68	0.70	0.70	0.74	0.76
Maximum volume of sorption space W_S, cm^3/g	0.24	0.25	0.26	0.32	0.37
Macropore volume $V_{macro} = V_{\Sigma} - W_S$, cm^3/g	0.44	0.45	0.44	0.42	0.39
Strength $P_{\square}$, MPa	0.6	0.7	1.6	2.0	2.0
Bulk density Δ, g/cm^3	0.57	0.57	0.54	0.54	0.53

*The composition of the molding pastes differs for the samples presented in Table 3: from sample 1 to 5, the content of hydroxide powder increases from 20 to 100 wt % (with regards to $A1_2O_3$) and the amount of polyvinyl alcohol (depending on the content of hydroxide powder) increases from 0.0054 to 0.027 g of PVA per 1 g Al_2O_3, corresponding to a PVA content of 0.4 to 1.8 wt %.

sections exist on the desorption branches and the position of the lower point of the hysteresis loop, which depends on the nature of the adsorbent rather than the texture of the sample, corresponds to the value P/P_0 = 0.40 [16]. The textural characteristics of the synthesized carriers are shown in Table 5.

Based on the observations during the extrusion of molding pastes, it can be concluded that the use of PVA as a component of the dispersion medium leads to a decrease in the degree of liquefaction of the molding paste during extrusion by enveloping the bayerite particles, thereby preventing the release of colloid-bound water and allowing the production of granules of the η-$A1_2O_3$ carrier. The use of aluminum oxide powder in the preparation of molding pastes can, within certain limits, helps regulate the porous structure of the obtained carriers.

The results of carrier sample testing for the low-temperature isomerization of *n*-butane are presented in Table 6. A carrier based on η-$A1_2O_3$ obtained from a powder of bayerite structure aluminum hydroxide produced by Pural BT (*Sasol*, Germany) was used as a comparison control sample.

The test results of the carrier samples show that, regardless of the ratio of bayerite- and $A1_2O_3$-containing components used, the samples demonstrate comparable selectivity with the reference model.

An increase in the proportion of bayerite in the molding paste leads to an increase in all monitored indicators of the *n*-butane isomerization process. This may be due to the noted increase in the specific surface area of the carrier samples and the volume of large mesopores in the range of 20–40 nm. Thus, sample 5 provides the highest selectivity and conversion values in the process.

CONCLUSIONS

The influence of forming conditions on the textural characteristics and catalytic activity of the low-temperature isomerization catalyst η-aluminum oxide carriers were studied.

We determined that during the deposition of bayerite from an aluminum nitrate solution with ammonia under literature conditions [14], a precipitate with particle sizes from 0.2 to 50 µm was formed, with further heat treatment of the sample at 500°C leading to an increase in the particle size to 100 µm.

We found that using PVA as a component of the dispersion medium of the forming pastes from bayerite powder led to a decrease in the degree of separation of colloid-bound water from the interlayer space of bayerite, providing the capability of obtaining granules of η-Al_2O_3 by screw extrusion.

The granules of the η-Al_2O_3 carrier obtained by the screw extrusion of pastes of bayerite powder with PVA were characterized by the following textural characteristics: $S_{sp} = 365$ m$_2$/g, $V_{\Sigma} = 0.76$ cm^3/g, $W_s = 0.37$ cm^3/g, $V_{macro} = 0.39$ cm^3/g, mechanical strength $P_{\square} = 2.0$ MPa. The introduction of the η-Al_2O_3 powder as a heterogeneous additive in the bayerite molding paste, plasticized by PVA, allowed us to regulate the porous structure of the resulting carriers. Their textural characteristics changed.

Table 4. Size distribution of the volumes and surface areas of pores

Sample No.	Characteristic	Range of pore size, nm		
		3–10	10–50	50–80
1	d_{max}, nm	4.6	27.4	65.2
	Pore volume, cm^3/g	0.12	0.16	0.08
	Surface area, m^2/g	130	90	5
2	d_{max}, nm	4.4	30.5	67.2
	Pore volume, cm^3/g	0.12	0.16	0.08
	Surface area, m^2/g	130	95	5
3	d_{max}, nm	3.9	31.5	69.2
	Pore volume, cm^3/g	0.12	0.18	0.14
	Surface area, m^2/g	100	125	10
4	d_{max}, nm	3.9	31.5	71.3
	Pore volume, cm^3/g	0.13	0.21	0.15
	Surface area, m^2/g	110	150	10
5	d_{max}, nm	3.7	31.5	77.8
	Pore volume, cm^3/g	0.14	0.24	0.16
	Surface area, m^2/g	215	155	10

Table 5. Summary data table of the porous structure of synthesized carriers studied by nitrogen porosimetry at 77 K using an Autosorb 6iSA unit

Defined parameter	Sample No.				
	1	2	3	4	5
Specific surface, m^2/g	230	240	250	275	380
Pore volume, cm^3/g	0.39	0.48	0.38	0.54	0.53

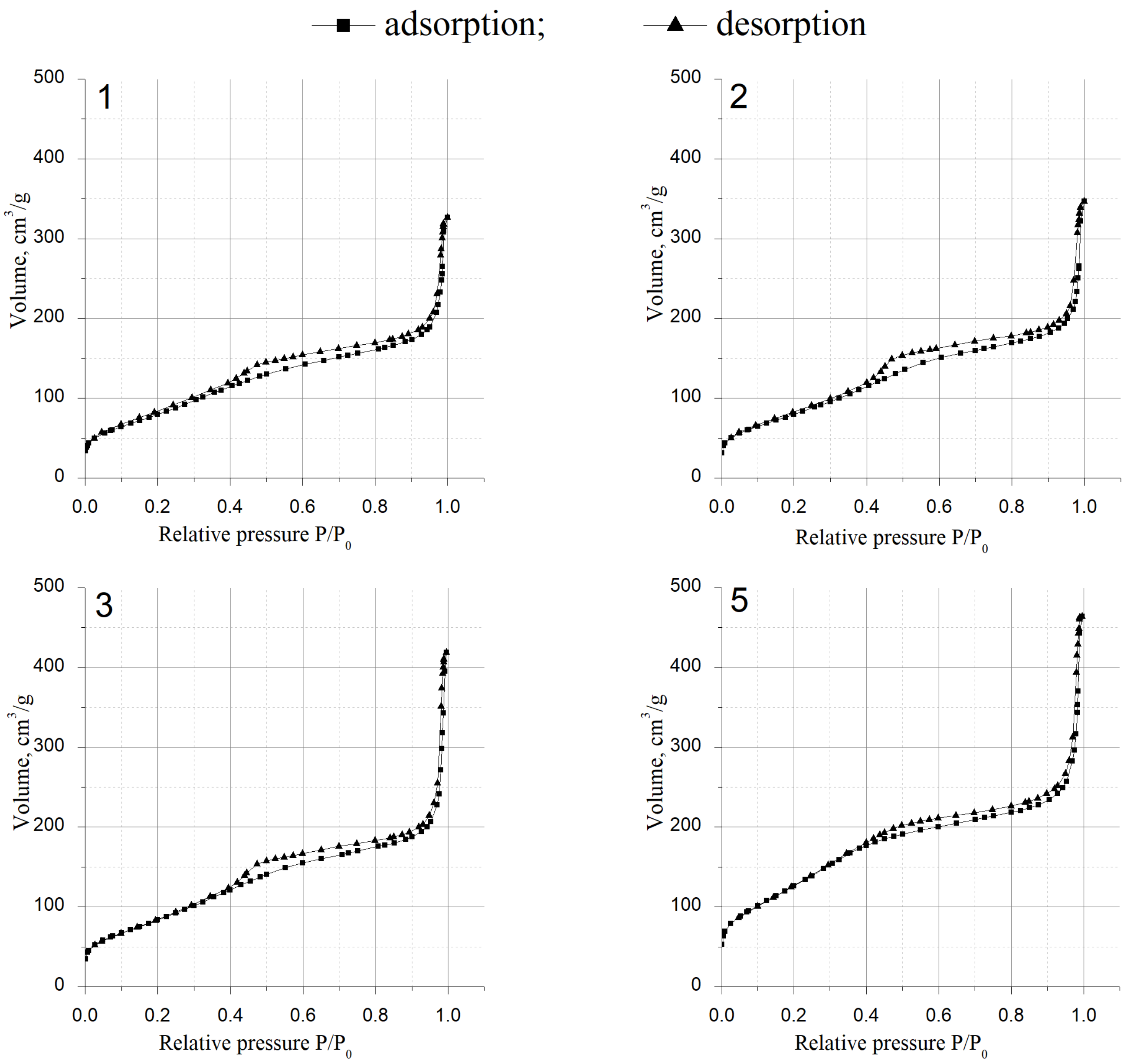

Fig. 5. Nitrogen adsorption-desorption isotherms at 77 K for synthesized carrier samples (the numbers on the graph corresponds to the sample number).

Table 6. Test results of the carrier samples for the low-temperature isomerization reaction of *n*-butane

Activity indicator	**Sample No.**					***Sasol***
	1	**2**	**3**	**4**	**5**	
Depth of isomerization *I*, %	17.0	20.5	20.9	21.3	21.4	21.8
Conversion of *n*-butane *K*, %	17.5	21.2	21.6	22	22.1	24.3
Selectivity *S*, %	94.5	94.8	95.3	95.3	95.6	94.4

Increasing the mass fraction of the powder in a mixture with bayerite to 80 mass % led to a decrease in the S_{sp} to 285 m^2/g, V_{Σ} to 0.68 cm^3/g, W_s to 0.24 cm^3/g, and an increase in the V_{macro} to 0.44 cm^3/g, with an unfortunately noticeable decrease in the mechanical strength of the $P_{\square}$ to 0.6 MPa. Increasing the PVA content in the molding paste from 0.4 to 1.8 wt % accompanied an increase in the ranges of the prevailing size of the secondary pores to values of 10–50 and 50–80 nm.

Tests of the carriers for catalytic isomerization of *n*-butane revealed that the samples, which are different in the ratio of the initial bayerite and Al_2O_3-containing components, have approximately equal and sufficiently high selectivity and are promising materials as catalysts for low-temperature isomerization of hydrocarbons.

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