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Optimization of the Composition of $Pt/B_2O_3–Al_2O_3$ Catalyst for Hydroisomerization of Benzene-Containing Fractions

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Abstract

The possibility to use available and easily synthesized borate-containing aluminium oxide as an acidic support for the catalyst of hydroisomerization of benzene-containing gasoline fractions was demonstrated for the first time. The phase composition, texture characteristics and acid properties of $B_2O_3–Al_2O_3$ systems with boron oxide content 0.9–39.0 mass %, obtained by mixing pseudoboehmite with solid *ortho*-boric acid followed by annealing at a temperature of 600 °C were studied. For hydroisomerization of the model mixture of n-heptane with benzene it was shown that the most efficient sample is $Pt/B_2O_3–Al_2O_3$ with the support containing 27.5 mass % of boron oxide. This catalyst provides almost complete benzene hydrogenation and the maximal yield of methylcyclopentane (12.1 mass %) and isoheptanes (43.5 mass %) at a temperature of 350 °C. Higher selectivity of isomerization reactions in this case is connected with the smaller amount of strong acid centres on the catalyst surface.

Key words: borate-containing aluminium oxide, hydroisomerization, decrease in benzene content

INTRODUCTION

In connection with tightening of ecological requirements, the development of the production of high-octane petrol with decreased concentrations of aromatic hydrocarbons, first of all benzene, becomes urgent. These technological include also hydroisomerization of benzene-containing fractions. This process involves consequent reactions of benzene hydrogenation and isomerization of the formed cyclohexane (CH) into methylcyclopentane MCP), which allows one to exclude a decrease in octane number.

Bifunctional systems are used as the catalysts of hydroisomerization. In these systems traditionally platinum or palladium act as hydrogenating component, while the acid function is played by zeolites, heteropolyacids or anion-modified zirconium dioxide [1–6]. The disadvantages of the above-described systems include the complexity of their preparation, high cost of the acid support and a limited temperature range for their use, which is not optimal for the achievement of the high yield of methylcyclopentane.

In the present work it is proposed to use borate-containing aluminium oxide as an acid support for the catalyst of hydroisomerization of benzene-containing petrol fractions; it is characterized by low cost and simplicity of preparation, as well as high stability under hydrothermal conditions and in reducing environment [7].

The goal of the present work was to study the effect of the chemical composition of borate-containing support on its physicochemical properties and to investigate the catalytic properties of bifunctional systems $Pt/B_2O_3–Al_2O_3$ in hydroisomerization of a model mixture of n-heptane and benzene.

EXPERIMENTAL

The initial components for the preparation of acid supports $B_2O_3–Al_2O_3$ (BA-x samples where x is the actual concentration of B_2O_3, mass %) were pseudoboehmite (manufactured by Promyshlennye Katalizatory JSC, Ryazan, Russia) and orthoboric acid. Pseudoboehmite was mixed with solid *ortho*-boric acid the amount of which was determined depending on the required concentration of B_2O_3 in the resulting support (Table 1). Then the mass was partially evaporated with a water bath under periodic mixing and dried at 120 °C for 16 h. The dried material was ground and annealed in a muffle at a temperature of 600 °C for 16 h. A distinguishing feature of this method of the synthesis of $B_2O_3-Al_2O_3$ systems is the use of orthoboric acid in the solid form which maximally simplifies the procedure of support preparation. Aluminium oxide (sample A) obtained by annealing pseudoboehmite at a temperature of 600 °C for 16 h was used for comparison. To obtain difunctional catalysts (Pt/BA-x and Pt/A samples) the supports were impregnated with the solution of H_2PtCl_6 according to water-absorbing capacity to achieve platinum concentration in final samples at a level of 0.3 mass %, dried at 120 °C and annealed at 500 °C.

The concentration of boron oxide in the annealed $B_2O_3-Al_2O_3$ samples was determined by means of AES-ICP with a Varian 710-ES spectrometer.

Thermal analysis of the hydroxide precursors of supports (after drying at 120 °C) was carried out using a Netzsch STA 449 C instrument in the flow of gas mixture containing 20 vol. % O_2 + 80 vol. % Ar within temperature range 25–1000 °C at the heating rate of 10 °C/min.

X-ray phase analysis was carried out using a Bruker D8 Advance diffractometer in monochromatic CuK_α radiation ($\lambda = 1.5418$ nm). The samples were scanned within angle range $2\theta = 5-80$ deg with a step of 0.1°and accumulation time 7 s in each point at room temperature. The diffraction patterns were interpreted with the help of EVA (Bruker) software using the ICDD PDF-2 powder diffraction database (the version of 2006). The average size of coherent regions (coherent length) was calculated using Selyakov–Sherrer equation.

Nitrogen adsorption-desorption isotherms were recorded with a Micromeretics'ASAP-2020 analyzer. The range of equilibrium relative pressures P/P_0 was from 10^{-5} up to 0.996. Before carrying out adsorption measurements, all the samples were pumped at 300 °C for 6 h. Calculations of specific surface according to BET (S_{sp}) were carried out within the range of equilibrium relative pressure of nitrogen gas 0.05–0.25 from the adsorption isotherm. Pore volume (V_{por}) was determined from the value of nitrogen adsorption at the equilibrium relative pressure equal to 0.990.

The samples were studied by means of IR spectroscopy with a Shimadzu IR Prestige-21 instrument. For this purpose, the samples were pressed in tablets without a binder, with a thickness of 0.010–0.025 g/cm^2, and annealed in vac-

TABLE 1

Chemical composition, texture characteristics and coherent length for support samples with different boron oxide concentrations

Samples*	B_2O_3 concentration, mass %		S_{sp}, m^2/g	V_{por}, cm^3/g	Coherent length of Al_2O_3, nm
	nominal	actual			
A	–	–	190	0.44	7.0
BA-0.9	1.0	0.9	229	0.46	6.2
BA-2.7	3.0	2.7	265	0.46	5.6
BA-4.4	5.0	4.4	281	0.46	5.1
BA-9.3	10.0	9.3	287	0.46	4.1
BA-13.9	15.0	13.9	243	0.41	3.0
BA-17.3	20.0	17.3	204	0.38	2.0
BA-27.5	30.0	27.5	128	0.28	2.0
BA-39.0	40.0	39.0	58	0.18	–

* Here and in Table 2: numbers in sample designations correspond to the actual concentration of B_2O_3 in the support, mass %.

uum at a temperature of 400 °C for 2 h. The spectra were recorded at room temperature within wavenumber range 400–4000 cm^{-1} (resolution 4 cm^{-1}) with accumulation and averaging of the results of 50 measurements. The spectra of adsorbed CO were recorded at room temperature.

Thermoprogrammed desorption (TPD) of ammonia was carried out with an AutoChem-2920 analyzer (Micromeritics). A mixture of 10 vol. % NH_3 in helium was used for experiments. The rate of flow through the reactor with the sample was 25 cm^3/min. Before experiment, the sample was blown with helium at 550 °C for 1 h, and then cooled in He flow to a temperature of 100 °C. Adsorption of NH_3 was carried out at the same temperature for 1 h, and then the sample was blown with helium to remove physically adsorbed ammonia for 1 h. The TPD process with ammonia was carried out within temperature range 100–550 °C with the rate of measuring cell heating 10 °C/min. For the spectrum to reach the baseline, the sample was kept at a temperature of 550 °C.

Hydroisomerization of a model mixture of *n*-heptane with benzene (80 mass %) was carried out in a static bed reactor at a pressure of 1.5 MPa, mass rate of liquid raw material supply (MRLMS) 3.0 h^{-1}, molar ratio of hydrogen/raw material equal to 5, and at a temperature of 350 °C. Before the start of experiments, catalyst samples were activated in hydrogen flow at 400 °C. The composition of products was analyzed on line using a Khromos GKh-1000 gas chromatograph equipped with a capillary column (100 m long, DB-1 phase) and flame ionization detector. Calculating the parameters of hydroisomerization we took into account the amount of oxygen absorbed in the process. The equations to calculate transformation degree of initial hydrocarbons, yields and selectivity of the formation of reaction products are reported in [5].

RESULTS AND DISCUSSION

High-temperature region is more favourable for the reaction of cyclohexane isomerisation into methylcyclopentane which is the basis for the compensation of the losses of octane number. This is connected with the fact that the thermodynamic stability of MCP in comparison with CH increases with temperature rise. According to the data reported in [4], the equilibrium ratio MCP/CH at 250 °C is 3.7, while at 300 °C it is 5.2 and reaches 6.7 at 350 °C. The known data on the acid properties and catalytic activity of borate-containing aluminium oxide in alcohol dehydration [9, 10], alkene isomerisation [11, 12] and butane oligomerization [13, 14] point to the potential promising character of its use as a support for the catalyst of hydroisomerization of benzene-containing fractions.

In our work, we obtained eight samples of $B_2O_3-Al_2O_3$ supports with boron oxide content 0.9–39 mass % (see Table 1). The reference sample was pure aluminium oxide. One can see that the data on the actual and nominal concentration of boron oxide in $B_2O_3-Al_2O_3$ samples are in good agreement with each other. This means that almost the whole boron introduced at the stage of synthesis remains in the system after thermal treatment.

Three major regions of mass loss are observed in the DTG curves of hydroxide precursors (Fig. 1, *a*). The removal of physically adsorbed water occurs below 200 °C. The peaks in the region of 250–330 and 350–530 °C characterize dehydration of pseudoboehmite and crystallization of γ-Al_2O_3, respectively [15]. According to DTA data, they are accompanied by endothermic effects (see Fig. 1, *b*). For the hydroxide precursor of BA-39.0 sample, mass loss within temperature range 150–225 °C is observed, accompanied by the corresponding endothermic effect. These points to the presence of a substantial amount of free boric acid in the system. It is decomposed within this temperature range. With an increase in the concentration of boron oxide in the system $B_2O_3-Al_2O_3$, the peak of mass loss characterising the formation of γ-Al_2O_3 crystal phase becomes diffuse and shifts to the higher temperature range, which is connected with slowing down of the process of aluminium oxide crystallization. The DTA curves of the samples with boron oxide concentration 9.3 mass % and above contain exothermal peaks within temperature range 700–950 °C; these peaks correspond to the formation of crystal aluminoborates [16]. With an increase in boron oxide concentration in the samples from 9.3 to 39.3 mass % we observe a shift of the maximum of this peak from 920 to 725 °C.

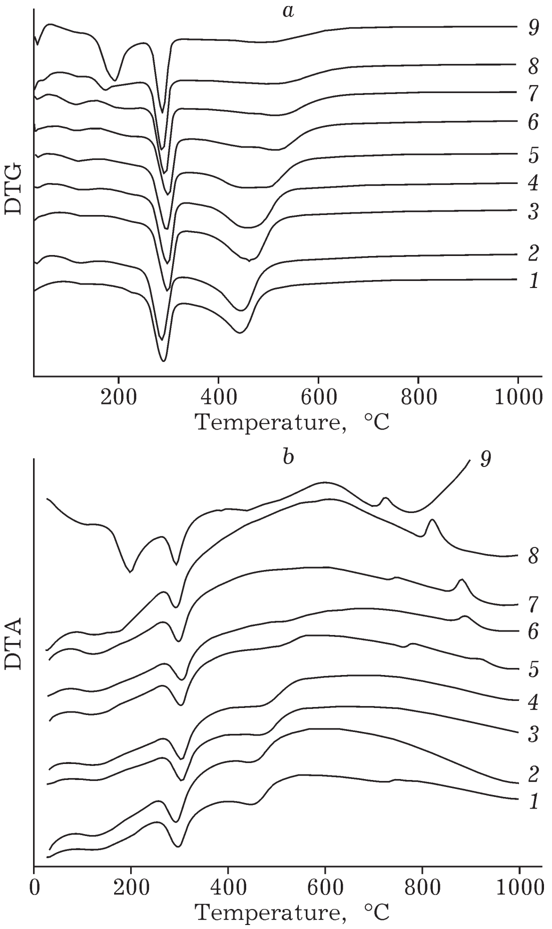

Fig. 1. DTG *(a)* and DTA (*b*) curves of hydroxide precursors of the samples of oxide supports: *1* – A, *2* – BA-0.9, *3* – BA-2.7, *4* – BA-4.4, *5* – BA-9.3, *6* – BA-13.9, *7* – BA-17.3, *8* – BA-27.5, *9* – BA-39.0. Here and in Fig. 2: numbers in sample title mean the concentration of B_2O_3, mass %.

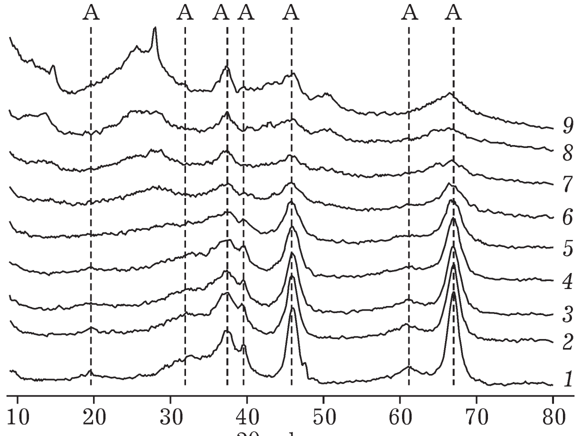

Fig. 2. Diffraction patterns of the samples of oxide supports with different concentrations of boron oxide: *1* – A, *2* – BA-0.9, *3* – BA-2.7, *4* – BA-4.4, *5* – BA-9.3, *6* – BA-13.9, *7* – BA-17.3, *8* – BA-27.5, *9* – BA-39.0; A – reflections corresponding to the γ-Al_2O_3 phase. For designations, see Fig. 1.

Diffraction patterns of the samples of oxide supports (Fig. 2) contain reflections that are characteristic for the γ-Al_2O_3 phase. With an increase in the concentration of boron oxide in the system B_2O_3–Al_2O_3 gradual broadening and a decrease in the intensity of γ-Al_2O_3 samples occur, which points to an increase in the fraction of amorphous phase in the samples [17]. The size of primary γ-Al_2O_3 particles decreases (see Table 1). So, according to the data of X-ray phase and thermal analyses, the introduction of boron acid into boehmite hinders crystallization of aluminium oxide. However, the effect of slowing-down of aluminium oxide crystallization is exhibited to a less extent for B_2O_3–Al_2O_3 samples obtained by mixing pseudoboehmite with solid *ortho*-boric acid because after thermal treatment the traces of γ-Al_2O_3 phase are detected till boron oxide concentration of 39.0 mass %. At the same time, B_2O_3–Al_2O_3 samples obtained by the treatment of aluminium hydroxide with the aqueous solution of H_3BO_3 are X-ray amorphous even when boron oxide concentration at a level of 10 mass % [18]. The diffraction patterns of B_2O_3–Al_2O_3 samples with boron oxide concentration 13.9 mass % and higher contain broad reflections in the angle region $2\theta = 12–17$ and 21–29 deg, which can point to the formation of dispersed aluminoborates or poorly crystallized phase B_2O_3 [19]. For BA-39.0 sample in this angle range 2θ the reflections around 14.5 and 28 deg are present, which may be related to B_2O_3 phase (PDF 13-0570).

Texture characteristics of oxide supports are presented in Table 1. One can see that the dependence of specific surface on the chemical composition of the system B_2O_3–Al_2O_3 has the extremal character. The maximal values of S_{sp} (281–287 m^2/g) correspond to the samples with the mass concentration of boron oxide 4.4–9.3 %. All samples containing up to 9.3 mass % B_2O_3 have close pore volume. With further increase in B_2O_3 content specific surface and pore volume decrease. This is likely connected with the fact that boron oxide melts during thermal treatment and fills the pore space of aluminium oxide [20, 21].

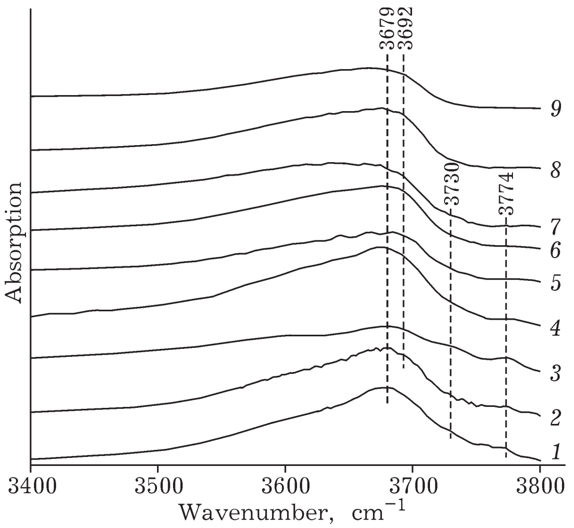

Fig. 3. IR spectra of the samples of supports within the range of hydroxyl group absorption: *1* – A, *2* – BA-0.9, *3* – BA-2.7, *4* – BA-4.4, *5* – BA-9.3, *6* – BA-13.9, *7* – BA-17.3, *8* – BA-27.5, *9* – BA-39.0. For designations, see Fig. 1.

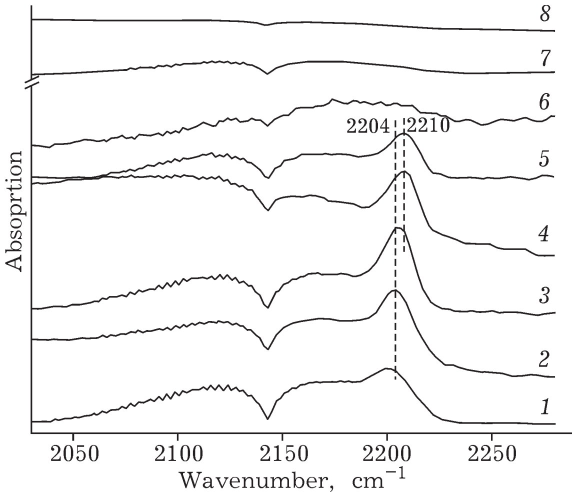

Fig. 4. IR spectra of adsorbed CO (10 Torr, 25 °C): *1* – A, *2* – BA-0.9, *3* – BA-2.7, *4* – BA-4.4, *5* – BA-9.3, *6* – BA-13.9, *7* – BA-17.3, *8* – BA-27.5. For designations, see Fig. 1.

Investigation of the samples by means of IR spectroscopy (Fig. 3) showed that there are three types of hydroxyl groups on the surface of aluminium oxide (sample A); the absorption bands at 3679, 3730 and 3774 cm^{-1} in the IR spectra correspond to these types of groups. According to the data of [10], these groups have acidic, neutral and basic character, respectively. The former two bands characterize bridging OH groups in the asymmetric surroundings (absorption band at 3639 cm^{-1} corresponds to Al_o–O(H)–Al_t where Al_o and Al_t are aluminium ions in octahedral and tetrahedral coordinations, respectively) and in the symmetric surroundings (absorption band at 3730 cm^{-1} corresponds to Al_o–O(H)–Al_o) [22]. The absorption band at 3774 cm^{-1} relates to the terminal OH groups bound with aluminium cation in tetrahedral coordination [22]. Modification of aluminium oxide with boron leads to the appearance of absorption band at 3692 cm^{-1}. This band characterizes B–OH groups [10, 12]. The presence of these groups defines the formation of Brønsted acidity in borate-containing aluminium oxide [16]. The introduction of B_2O_3 into aluminium oxide at a level of 13.9 mass % leads to the disappearance of terminal OH groups (see Fig. 3).

After adsorption of CO, the IR spectra of aluminium oxide and B_2O_3–Al_2O_3 samples containing 0.9 to 9.3 mass % B_2O_3 contain absorption peaks with the frequencies 2204–2210 cm^{-1} (Fig. 4), corresponding to CO complexes with Lewis acid centres (LAC) of medium force [22]. With an increase in boron oxide concentration to 13.9 mass %, these bands disappear.

So, the introduction of B_2O_3 into aluminium oxide is accompanied by the formation of Brønsted acid centres (BAC) on the surface. With an increase in boron oxide concentration in the system B_2O_3–Al_2O_3, a transition from acid-base character of the surface to the acid one occurs. No LAC remains on the surface of the support.

Estimation of the amount of acid centres on oxide supports was carried out by means of ammonia TPD (Table 2). The fractions of weak, medium and strong acid centres were determined calculating the area under the TPD curve within temperature ranges up to 250, 250–350 and 350–550 °C, respectively. According to the data obtained, the dependence of the number of acid centres on boron content in the system B_2O_3–Al_2O_3 passes through a maximum which is achieved for B_2O_3 content at a level of 9.3–13.9 mass %. The total amount of acid centres increases by about 60 rel. % in comparison with non-modified aluminium oxide. The dependencies of the amount of weak, medium and strong acid centres on the chemical composition of the system B_2O_3–Al_2O_3 have the extremal character, too. The introduction of relatively small amount of B_2O_3 (2.7–4.4 mass %) into aluminium oxide to a higher extent pro-

TABLE 2

Acidity of the samples of supports according to the data of ammonia TPD

Samples	Amount of acid centres, μmol NH_3/g			
	Weak (up to 250 °C)	Medium (250–350 °C)	Strong (350–550 °C)	Total
A	66	108	110	284
BA-0.9	71	118	126	316
BA-2.7	74	126	142	342
BA-4.4	88	151	172	411
BA-9.3	108	167	178	453
BA-13.9	117	173	169	458
BA-17.3	106	152	150	408
BA-27.5	109	133	106	349
BA-39.0	99	136	88	322

Note. For designations, see Table 1.

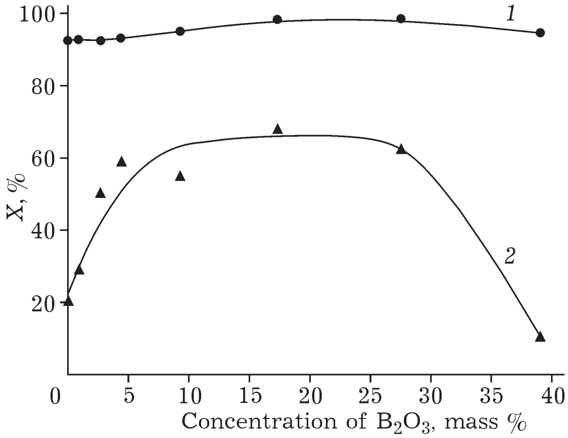

Fig. 5. Effect of boron oxide concentration in the system $Pt/B_2O_3–Al_2O_3$ on the transformation degree (*X*) of initial components of the mixture *n*-heptane–benzene at a temperature of 350 °C: *1* – benzene, *2* – *n*-heptane.

motes an increase in the number of strong acid centres. Further increase in B_2O_3 content promotes an increase in the concentration of weak acid centres and the acid centres of medium force. For example, for the samples containing 27.5–39.0 mass % boron oxide, lower concentration of strong acid centres is typical, even in comparison with pure aluminium oxide.

In order to choose optimal catalyst, we carried out an investigation of the properties of $Pt/B_2O_3–Al_2O_3$ samples of different chemical composition in the reaction of hydroisomerization of the model mixture of *n*-heptane and benzene. Platinum concentration in bifunctional catalysts of Pt/BA-*x* series and in Pt/A sample was 0.3 mass %. According to the data obtained (Fig. 5), the maximal degree of benzene transformation at a temperature of 350 °C is 98.5–98.7 % and is achieved with PtPt/BA-17.3 and Pt/BA-27.5 samples. For all the other samples, the degree of benzene transformation varies within the range 92.5–95.2 %. With an increase in boron oxide concentration in the system $Pt/B_2O_3–Al_2O_3$ to 4.4 mass %, conversion of *n*-heptane increases, which is connected with an increase in the acidity of samples (see Table 2). In addition, the yield of hydrocarbon gases $C_1–C_4$ increases from 7.7 mass % to the

TABLE 3

Parameters of hydroisomerization of the model mixture of *n*-heptane with benzene at 350 °C

Samples	Yield, mass %				Selectivity, %		MCP/CH	$(C_1+C_2)/(C_3+C_4)$
	$C_1–C_4$*	C_{5+}*	MCP	*iso*-C_7	МЦП	*iso*-C_7		
Pt/A	7.7	94.0	0.3	1.1	1.8	5.8	0	0.4
Pt/BA-0.9	11.3	90.6	0.3	1.3	1.8	4.9	0.0	0.4
Pt/BA-2.7	21.6	80.6	0.5	2.0	2.7	4.4	0.0	0.3
Pt/BA-4.4	26.8	75.7	0.8	2.8	4.6	5.5	0.1	0.3
Pt/BA-9.3	22.8	79.5	3.0	9.8	16.2	21.9	0.3	0.2
Pt/BA-17.3	9.8	92.2	8.4	41.1	44.2	75.7	2.3	0.2
Pt/BA-27.5	5.1	96.6	12.1	43.5	63.4	86.8	3.1	0.1
Pt/BA-39.0	1.3	100.2	3.5	7.1	18.9	85.2	0.2	0

Note. For designations, see Table 1.

*Total yield of $C_1–C_4$ and C_{5+} hydrocarbons more than 100 % is connected with hydrogen absorption during reaction.

maximal value (26.8 mass %) for the whole series of samples under study (Table 3). With further increase in B_2O_3 content in samples from 4.4 to 27.5 mass %, the degree of n-C_7 transformation changes only weakly (see Fig. 5). At the same time, selectivity of hydroisomerization increases, which leads to a decrease in the yield of C_1–C_4 hydrocarbons and an increase in the yield of target products – methylcyclopentane and isoalkanes C_7 (see Table 3). An increase in the selectivity of target isomerization reactions may be explained in this case by the fact that the number of strong acid centres on the surface of the samples decreases with an increase in boron oxide concentration from 4.4 to 27.5 mass % (see Table 2); these centres are presumably responsible for the side hydrocracking reactions. In addition, a decrease in the ratio $(C_1 + C_2)/(C_3 + C_4)$ (see Table 3) points to a decrease in the intensity of cracking reactions on metal centres (hydrogenolysis), which also promotes an increase in the selectivity of isomerization.

The most efficient catalyst in the hydroisomerization of the model mixture of n-heptane with benzene is Pt/B_2O_3–Al_2O_3 with the support containing 27.5 mass % of boron oxide (sample Pt/BA-27.5). This catalyst provides the highest selectivity of the formation of MCP and isoheptanes and helps achieving the maximal yield of these products (see Table 3).

CONCLUSION

It was demonstrated that the preparation of B_2O_3–Al_2O_3 system through mixing pseudoboehmite with solid orthoboric acid and subsequent annealing at a temperature of 600 °C results in the interaction between the components of the system, which causes slowing-down of aluminium oxide crystallization. The introduction of boron oxide into aluminium oxide causes the appearance of Brønsted acid centres on the surface of the system and an increase in total acidity of the samples.

It was established in the studies of catalytic properties that the sample Pt/B_2O_3–Al_2O_3 with the support containing 27.5 mass % boron oxide is the most efficient catalyst for hydroisomerization of the model system of n-heptane and benzene. On the basis of the data on complete hydrogenation of benzene, high yields and selectivity of the formation of target products of hydroisomerization (methylcyclopentane and isoheptane) provided at this catalyst at a temperature of 350 °C, we may state that the application of this catalyst in hydroisomerization of real raw material is promising.

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