

Isomerization of *n*-Hexane on Binder-Free Shaped Platinum-Containing Mordenite

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Abstract—A catalyst has been prepared as binder-free shaped MOR-type zeolite in the H form promoted with 0.5 wt % platinum, and *n*-hexane conversion over this catalyst has been studied. It has been found that the selectivity for C₄–C₆ isoparaffins on the new catalyst is about 90% at 300°C, a feed space velocity of 1.5 h⁻¹, and a hydrogen pressure of 3 MPa, with the hexane conversion being 80.0–83.0 wt % and the selectivity for isohexane making 83.0–86.0%. It has been shown that the new catalyst is stable for 50 h on-stream under these conditions.

Keywords: MOR type zeolite, pellets, catalyst, isomerization, *n*-hexane

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Heterogeneous catalytic isomerization of normal C₅–C₆ paraffins is becoming increasingly important in the production of motor fuels. In addition, isomerization of pentane is used in the production of isoprene by two-step dehydrogenation of isopentane [1, 2]. One of the catalysts used in industrial hydroisomerization processes of light paraffins is the bifunctional catalyst consisting of a MOR-type zeolite in the H form and 0.4–0.6 wt % platinum [3]. The catalyst also contains 30 wt % γ -Al₂O₃ as a binder, the presence of which lowers the concentration of strong acid sites to almost the same extent.

Gorshunova et al. [4] described a process for preparing granulated MOR type zeolite without a binder (MOR-BF) in the Na form to have the porous structure made by not only micro-, but also meso- and macropores. It may be assumed that the catalyst based on this zeolite will have a higher concentration of catalytically active sites as compared with catalysts in which the zeolite was shaped with a binder. In addition, the MOR-BF zeolite pellets are much stronger, since they are ensembles of intergrown crystals. This study is devoted to the synthesis of a novel *n*-paraffin isomerization catalyst on the basis of this crystalline aluminosilicate and testing it in the conversion of *n*-hexane under hydrogen pressure at different temperatures and feed space velocities.

EXPERIMENTAL

Powdered MOR-type zeolite and MOR-BF zeolite (pellets of a 1.6–2 mm diameter and a 3–6 mm

length) in the Na form was synthesized according to the procedure described in [4, 5] in a 5-L crystallizer autoclave equipped with a gate stirrer (60 rpm), electric heating, and a sampler. The silica ratio (SiO₂/Al₂O₃) of both zeolites was 10.

Samples of these zeolites with different degrees of decationation were prepared by ion exchange in an aqueous solution of ammonium nitrate at $T = 80$ – 90°C , a ratio of NH₄⁺ cations in the solution to Na⁺ cations in the zeolite of $G = 1.5$ g-equiv/g-equiv, pH = 5.5–7.0, and a duration of $\tau = 1$ h followed by heat treatment in air at 540–650°C for 4–6 h. The degree of exchange of Na⁺ for H⁺ (α_{Na}) above 0.7 was achieved as a result of several exchange treatments without intermediate calcination.

Procedures for determining the chemical and phase compositions, equilibrium adsorption capacity (mg/g) of zeolite for water vapor ($A_{\text{H}_2\text{O}}$) and benzene ($A_{\text{C}_6\text{H}_6}$), pore volume (V_{pore} , cm³/g), and specific surface area (S_{sp} , m²/g) are described elsewhere [4].

The acid properties of the aluminosilicates were studied using the technique of ammonia temperature-programmed desorption (TPD) [6].

Transformations of *n*-hexane on the catalytic systems obtained in this way were studied in a flow reactor with a catalyst charge of 5 cm³ at 250–400°C, an *n*-C₆H₁₄ feed space velocity of 1–3 h⁻¹, and a hydrogen pressure (P_{H_2}) of 3.0 MPa and flow rate of 1300–1700 L/(L_{cat} h). The choice of *n*-hexane as a

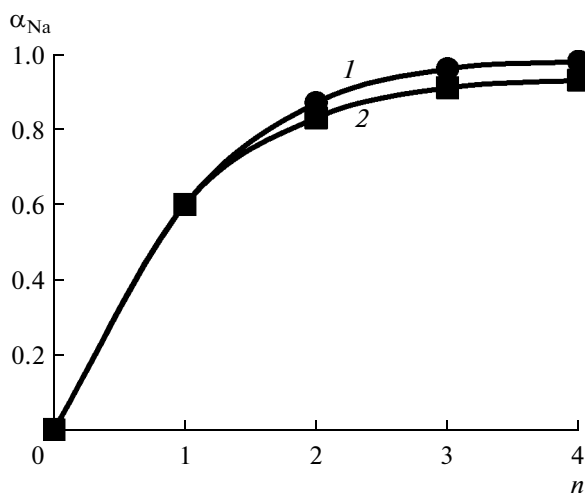


Fig. 1. Effect of the number of exchanges (n) on the degree of exchange of Na^+ for NH_4^+ cations (α_{Na}) in (1) powdered mordenite and (2) MOR-BF zeolite.

model feedstock was due to the fact that its content in gasoline fractions can be as high as 20–25 wt %.

The gaseous and liquid products of the reaction were analyzed using the technique of gas–liquid chromatography. Gaseous hydrocarbons were determined on a stainless steel column of a 6 m length and a 3 mm diameter packed with 10% SE-30-coated Chromosorb W (60–80 mesh). The liquid products were determined on a capillary column of a 50 m length (phase SE-30). Analyses were performed on a Chrom-5 chromatograph with a flame ionization detector in the temperature-programmed mode from 70 to 180°C at a heating rate of 4°C/min.

RESULTS AND DISCUSSION

The Na form of any zeolite is deprived of strong acid sites [7]. They appear after replacing the Na^+ cations primarily by H^+ cations. The H form of a zeolite of a particular structural type is most frequently obtained by substituting NH_4^+ cations from an aqueous solution of an ammonium salt for the Na^+ cations and the subsequent thermal treatment under the conditions specified above.

Figure 1 shows the dependence of α_{Na} in samples of zeolite MOR-BF and powdered mordenite on the number of ion-exchange treatments.

It is seen that the exchange is slower in the zeolite MOR-BF than in the powdered zeolite and the residual sodium content after four exchange treatments is higher by approximately 10% rel. The main reason behind the lower value of α_{Na} in the NaMOR-BF zeolite is that its pellets are intergrown crystals and part of the intracrystalline space remains inaccessible to exchange cations. It should be noted that an increase in the number of exchange runs over four does not lead to a further decrease in the residual sodium content.

Table 1 shows values for the pore volume and the “apparent” specific surface area according to the nitrogen low-temperature adsorption and desorption data, as well as equilibrium adsorption capacities for water vapor and benzene of the MOR-BF zeolite before and after ion-exchange treatments. For comparison, the relevant data for the sample of powdered mordenite are given. It can be seen that the replacement of Na^+ by H^+ cations increases both the pore volume and the “apparent” specific surface area. As a consequence, the equilibrium adsorption capacities for water and benzene vapors increase.

The influence of the α_{Na} value on the amount of strong acid sites (C_{NH_3} , mol/g, the amount of ammonia desorbed in the temperature range of 350–550°C) in the MOR-BF zeolite is illustrated in Fig. 2.

It is seen that as α_{Na} increases from 0.6 to 0.93, both the concentration of strong acid sites and their accessibility for benzene and heptane molecules increase. The incorporation of 0.5 wt % Pt into the porous structure of the samples with different values of α_{Na} does not have an appreciable effect on their acid properties.

Preliminary experiments showed that the conversion of n -hexane on the MOR-BF zeolite in the H form in a hydrogen atmosphere at 250°C and above largely results in the formation of cracking products, aromatic hydrocarbons, and coke. At the same time, the selectivity for C_6H_{14} isomers is not high. Therefore, the further experiments were carried out in the presence of the bifunctional catalyst 0.5Pt/HMOR-BF.

Figure 3 presents the results of examination of the effect of temperature on the conversion of n -hexane in

Table 1. Pore volume V_{pore} (cm^3/g), apparent surface area S_{sp} (m^2/g) by nitrogen adsorption, $A_{\text{H}_2\text{O}}$ (mg/g), and $A_{\text{C}_6\text{H}_6}$ (mg/g) of MOR zeolite samples before and after ion exchange

Sample	Degree of exchange of Na^+ for H^+	V_{pore}	S_{sp}	$A_{\text{H}_2\text{O}}$	$A_{\text{C}_6\text{H}_6}$
MOR-BF in the Na form	—	0.20	248	130	110
MOR-BF after 4 exchanges	0.93	0.23	345	150	120
Powdered mordenite in the Na form	—	0.15	278	150	130
Powdered mordenite after 4 exchanges	0.98	0.16	393	160	140

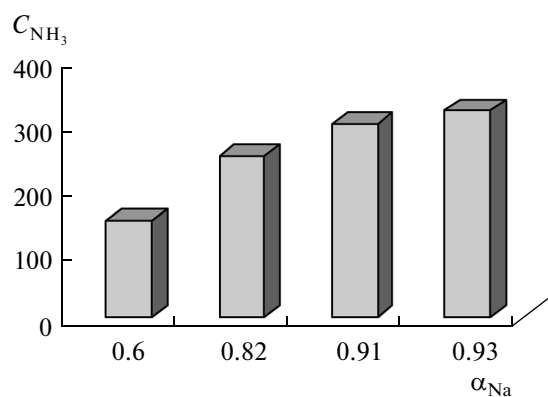


Fig. 2. Influence of the degree of exchange of Na^+ for H^+ cations (α_{Na}) on the amount of strong acid sites (C_{NH_3} , $\mu\text{mol/g}$, amount of ammonia desorbed in the temperature range of 350–550°C) in MOR-BF zeolite.

the presence of 0.5Pt/HMOR-BF at $P_{\text{H}_2} = 3.0$ MPa and $W = 1.5$ h⁻¹. It is seen that the *n*-hexane conversion is about 62.0 wt % even at 250°C. Elevation of temperature increases the conversion to an almost 100% level at 400°C.

A comparison of the conversion values for *n*-hexane in the H_2 medium and in the absence of hydrogen shows that the catalyst is more active in the former case. This is presumably due to the fact that the catalyst almost does not undergo deactivation during the first 2 h on stream at $P = 3.0$ MPa. It should be noted that the products of *n*-hexane conversion in the hydrogen atmosphere contain neither olefins nor aromatics in noticeable amounts. The results suggest that the isomerization of *n*-hexane on the 0.5Pt/HMOR-BF catalyst follows the classical bifunctional mechanism [1].

Table 2 shows the effect of temperature on the selectivity for the products of *n*-hexane conversion under the above conditions. It can be seen that at temperatures up to 300°C, the catalyst is active predominantly in the isomerization of *n*-hexane. As the temperature increases, the contribution of the cracking reaction increases.

The composition isohexanes produced on the 0.5Pt/HMOR-BF catalyst at different temperatures is given in Table 3.

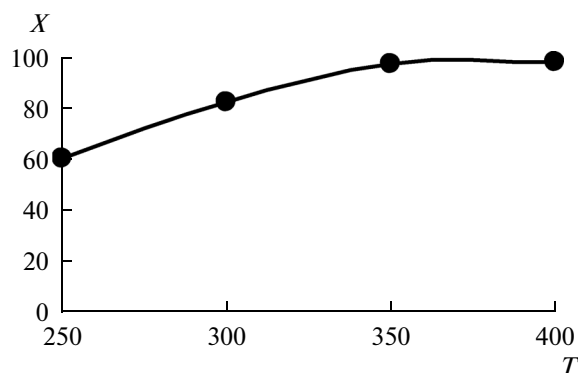


Fig. 3. Effect of temperature (T , $^{\circ}\text{C}$) on the conversion (X , wt %) of *n*-hexane over the 0.5Pt/HMOR-BF catalyst ($P = 3.0$ MPa, $W = 1.5$ h⁻¹, $\tau = 2$ h).

It is seen that 2- and 3-methylpentane make almost 80% of the composition. As the temperature increases from 250 to 350°C, the ratio of mono- to disubstituted isomers is not altered. A further increase in temperature to 400°C leads to an increase in the contribution of cracking reactions, and the disubstituted isomers are not found in the products of catalytic conversion of *n*-hexane. Note that similar results on the qualitative and quantitative composition of isomers were obtained earlier in other catalytic systems containing mordenite [8, 9].

An analysis of these data leads to the conclusion that a fairly high level of *n*-hexane conversion with a high isomerizing activity of zeolite catalysts is achieved at 300°C.

The results of examination of the effect of the feed space velocity on the conversion of *n*-hexane are shown in Fig. 4a.

It is seen that an increase in the space velocity from 0.75 to 3.0 h⁻¹ decreases the total conversion as a result of shortening the time of feedstock contact with the catalyst surface. But the selectivity for isohexanes (yield on an *n*-hexane converted basis) increases. The maximum yield on an *n*-hexane fed basis is observed at $W = 1.5$ h⁻¹.

Thus, in the presence of the 0.5Pt/HMOR-BF catalyst at the conversion of *n*-hexane no less than 80 wt %, the maximal selectivity for isohexanes (Fig. 4b) on the

Table 2. Effect of temperature on the selectivity for the products of *n*-hexane conversion in the presence of the 0.5Pt/HMOR-BF catalyst at $P = 3.0$ MPa, $W = 1.5$ h⁻¹, and $\tau = 2$ h

Temperature, $^{\circ}\text{C}$	Selectivities of formation (yields on <i>n</i> -hexane converted basis), %						
	<i>i</i> -C ₄	<i>n</i> -C ₄	<i>i</i> -C ₅	<i>n</i> -C ₅	<i>i</i> -C ₆	C ₆₊	C ₁ -C ₃
250	8.0	1.5	1.1	1.8	1.0	86.0	0.6
300	8.4	1.9	1.9	2.2	1.3	84.0	0.7
350	17.8	19.8	6.2	11.4	4.5	39.8	0.5
400	43.0	21.9	9.1	7.3	5.3	8.0	5.4

Table 3. Composition of isohexanes produced at various temperatures in the presence of 0.5Pt/HMOR-BF catalyst at $P = 3.0$ MPa, $W = 1.5$ h⁻¹, and $\tau = 2$ h

Temperature, °C	2,2-Dimethylbutane	2,3-Dimethylbutane	2-Methylpentane	3-Methylpentane
250	12.9	7.8	52.1	27.2
300	12.5	7.0	52.6	27.8
350	13.4	6.7	51.8	28.1
400	—	—	17.5	82.5

Table 4. Influence of *n*-hexane isomerization duration on the hexane conversion (X , wt %), selectivity for isohexanes (S , %), and the coke yield (C_c , % of catalyst weight); 0.5Pt/HMOR-BF, $T = 300^\circ\text{C}$, $P = 3.0$ MPa, $w = 1.5$ h⁻¹

Time, h	2	10	20	30	40	50
X	82.9	80.9	81.8	83.0	81.9	82.5
S	83.5	84.2	83.0	83.4	85.5	83.1
C_c	0.01	0.02	0.02	0.03	0.03	0.03

order of 84.0% is achieved at 300°C and a feed space velocity of 1.5 h⁻¹.

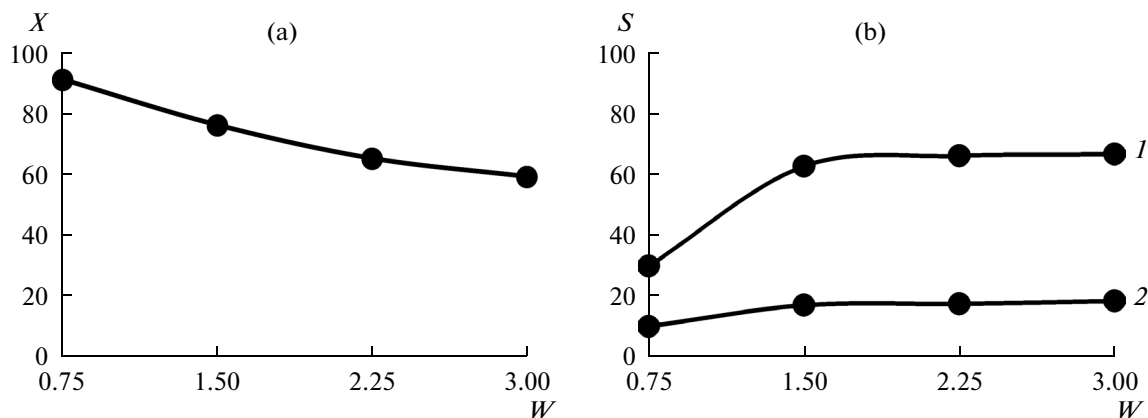
The catalytic properties of the 0.5Pt/HMOR-BF catalyst in the conversion of *n*-hexane was compared with those of the pelletized catalyst prepared by mixing 70.0 wt % mordenite in the H form (silica ratio 10) with AlO(OH) in an amount of 30.0 wt % (in terms of Al₂O₃) followed by shaping, thermal treatment at 600°C (AlO(OH) is converted to γ -Al₂O₃), and deposition of 0.5 wt % Pt on the resulting pellets (hereinafter, 0.5Pt/HMOR with a binder). A comparison of the results obtained on both samples (Figs. 4, 5) shows that the same values of *n*-hexane conversion are achieved at higher space velocities on the 0.5Pt/HMOR-BF catalyst (Fig. 4a) than over the catalyst with the binder (Fig. 5a).

Consequently, the catalyst prepared by using the MOR-BF zeolite is more active. However, the selectivities for isohexanes are close (Figs. 4b, 5b).

To assess the stability of the catalytic properties of 0.5Pt/HMOR-BF, experiments were conducted for 50 h (Table 4).

It was found that at 300°C and a feed space velocity of 1.5 h⁻¹, the conversion of *n*-hexane remained almost unchanged at the level of 80.0–83.0 wt % throughout the test time. The selectivity for isohexanes was 83.0–86.0%.

In summary, the catalysts based on MOR-BF zeolite have been synthesized and their physicochemical properties have been investigated. It has been found that the concentration of strong acid sites and their accessibility to some molecules, such as benzene and heptane, increase with an increase in the degree of exchange of Na⁺ for H⁺ cations from 0.6 to 0.93. It has

**Fig. 4.** Effect of feed space velocity (W , h⁻¹) on (a) the conversion (X , wt %) of *n*-hexane and (b) selectivity (S , %) for (1) methylpentanes and (2) dimethylbutanes in the presence of the 0.5Pt/HMOR-BF catalyst ($T = 300^\circ\text{C}$, $P = 3.0$ MPa, $\tau = 2$ h).

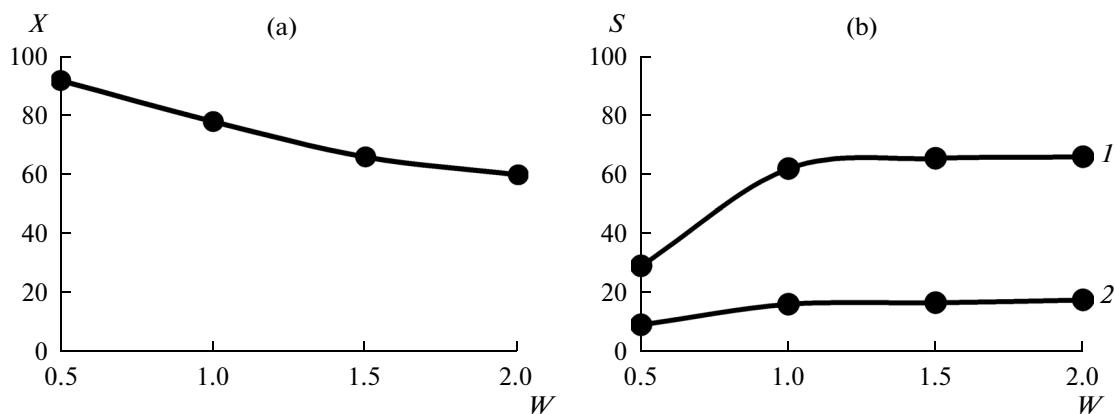


Fig. 5. Effect of feed space velocity (W , h^{-1}) on (a) the conversion (X , wt %) of *n*-hexane and (b) selectivity (S , %) for (1) methylpentanes and (2) dimethylbutanes on the catalyst 0.5Pt/HMOR with a binder ($T = 300^\circ\text{C}$, $P = 3.0$ MPa, $\tau = 2$ h).

been shown that in the absence of hydrogen in the gas phase, the maximal selectivity for C_4 – C_{7+} isoparaffins is 46.0–47.0% with an *n*-hexane conversion of 74.0–76.0 wt % at 300°C and a feed space velocity of 1 h^{-1} .

It has been found that on the new catalyst at 300°C , feed space velocity of 1.5 h^{-1} , and a hydrogen pressure of 3 MPa for 50 hours of testing, the selectivity for C_4 – C_6 isoparaffins is about 90%, with the *n*-hexane conversion being 80.0–83.0 wt % and the selectivity for isohexanes making 83.0–86.0%.

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