Isomerization of *n*-pentane and *n*-hexane on modified zeolites

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The activity and selectivity of catalysts based on TsVM (an analog of ZSM-5), Beta, and La-H-Beta zeolites modified by Pt, Pt—Fe, and Pt—Ga were studied in the isomerization of C_5 and C_6 linear alkanes. The Pt/HTsVM, Pt/H-Beta, and Pt/La-H-Beta catalysts are efficient in *n*-pentane isomerization, whereas the Pt/H-Beta and Pt/La-H-Beta are most active in *n*-hexane isomerization. Nearly equilibrium isoparaffin yield at a selectivity of at least 95—96% is reached on these catalysts unlike other zeolite systems. The overall yield of 2,2- and 2,3-dimethylbutanes is 22 wt.%. The hexane isomers are not formed over the Pt/HTsVM catalyst due to the molecular-sieve properties of this type of zeolites.

Key words: zeolites, modified zeolites, *n*-pentane, *n*-hexane, isopentane, isohexanes, isomerization.

The appearance of highly efficient zeolite-based catalysts resulted in intensification of studies of normal alkanes' hydroisomerization.[1—8] Bifunctional catalysts based on large-pore zeolites with strong acidic sites[3—5] as well as mesoporous materials, strong solid acids, and heteropolyacids[9—13] are promising systems for isomerization of normal alkanes.

This work is aimed at the study of the effect of the pore structure of zeolites (TsVM, Beta, and La-Beta) and modifying additives (Fe, Ga) on the activity and selectivity of Pt—zeolite catalysts in the isomerization of *n*-pentane and *n*-hexane. The effect of the Pt concentration in H-Beta zeolite on the yields of mono- and disubstituted isomers of hexane was studied.

Experimental

High-silica zeolites TsVM and Beta with molar SiO_2/Al_2O_3 ratios of 42 and 25, respectively, were used as H-, NH_4-, and La-forms. Procedures for the preparation of H- and NH_4-forms of zeolites and catalysts on their basis has been described earlier.[14] The La-form of zeolite Beta was prepared by ion-exchange of NH_4^+ for La^{3+} at a three-fold excess of lanthanum ions in an aqueous solution at 80 °C. Platinum and modifying additives (Fe^{3+}, Ga^{3+}) were successively introduced from dilute aqueous solutions of $[Pt(NH_3)_4]Cl_2$ and the corresponding nitrates. The solution was stored at 80 °C for 3—4 h and evaporated on a rotor vaporizer. Samples were dried at 130 °C (3 h), calcined in an air flow at 450—500 °C (3 h), and reduced in a hydrogen flow at 350 °C for 1 h. The Pt concentration in the samples was 0.2—0.5 wt.% and that of the modifying additives was 1.5 wt.%.

The isomerization of *n*-pentane and *n*-hexane was carried out in a flow setup at 210—340 °C and an atmospheric pressure. The catalyst volume was 2—3 cm^3, the space velocity of hydrocarbon feeding was 1 h^{-1}, and the molar ratios H_2 : n-C_5H_{12} and H_2 : n-C_6H_{14} were 3 : 1 and 6 : 1, respectively. The reaction products were analyzed by GLC on columns with polymethylphenylsiloxane or isoquinoline on Celite C-22.

Results and Discussion

***n*-Pentane.** The data on *n*-pentane isomerization over zeolites modified with Pt and Pt—Fe are presented in Figs. 1 and 2. Isomerization is the main pathway of *n*-pentane conversion at 240—260 °C. The selectivity to isopentane achieves 95—98% under these conditions. Side reactions, *viz.*, cracking, hydrocracking, and disproportionation, occur along with isomerization, affording saturated C_1—C_4 hydrocarbons (predominantly propane) and C_6 hydrocarbons. The yield of the products of cracking and hydrocracking is at most 2 wt.%. These processes are significantly enhanced at reaction temperatures above 280—300 °C, resulting in a decrease in the selectivity to isopentane and an increase in the yield of light products up to 20 wt.%.

The maximum yields of isopentane over the Pt/HTsVM and Pt—Fe/HTsVM catalysts are 62.2 and 58.3 wt.% at selectivities of 95.7 and 89.7%, respectively. The Pt/HTsVM catalyst is most active in *n*-pentane isomerization at 240—250 °C and Pt—Fe/HTsVM is active at 280—290 °C (see Fig. 1).

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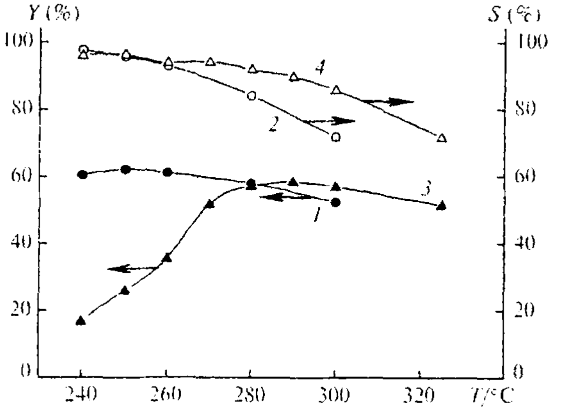

Fig. 1. The temperature effect on the yield (*Y*) of isopentane (*1*, *3*) and selectivity (*S*) in *n*-pentane isomerization (*2*, *4*) on the catalysts 0.5%Pt/HTsVM (*1*, *2*) and 0.5%Pt–1.5%Fe/HTsVM (*3*, *4*).

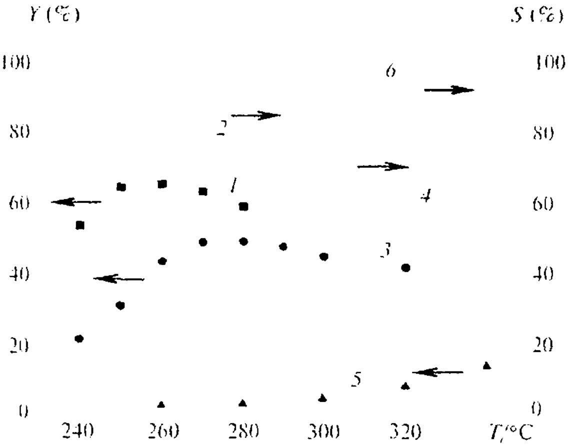

Fig. 2. The temperature effect on the yield (*Y*) of isopentane (*1*, *3*, *5*) and selectivity (*S*) in *n*-pentane isomerization (*2*, *4*, *6*) on the catalysts 0.5%Pt/H-Beta (*1*, *2*), 0.5%Pt–1.5%Fe/H-Beta (*3*, *4*), and 0.5%Pt/|Fe|-Beta (*5*, *6*).

The activity of the Pt-containing catalysts based on the H-Beta and La-H-Beta zeolites is comparable to that of Pt/HTsVM. The isopentane yields over Pt/H-Beta and Pt/La-H-Beta are 65.0 and 63.2 wt.% with selectivities of 98.2 and 97.8%, respectively. The yield of isopentane on the Pt–Fe/H-Beta catalyst is significantly lower than that in the presence of Pt–Fe/HTsVM and is at most 49 wt.% (see Fig. 2). The modification of Pt/H-Beta with Fe^{3+} cations likely leads to partial blocking of the acid sites of zeolite Beta, which are necessary for *n*-pentane isomerization, and the activity and selectivity of the catalyst decrease.

The Pt/|Fe|-Beta catalyst, in which Fe^{3+} cations were introduced during direct crystallization of the zeolite, is characterized by lower activity in *n*-pentane isomerization as compared to Pt- and Pt–Fe-modified zeolites with an aluminosilicate framework. The *n*-pentane conversion over this sample at 240–340 °C is at most 16% and the isopentane yield is 14 wt.%.

Thus, the yield of isopentane on the catalysts under study changes in the following sequence:

Pt/H-Beta ≈ Pt/HTsVM > Pt–Fe/HTsVM >
> Pt–Fe/H-Beta >> Pt/|Fe|-Beta.

***n*-Hexane.** The yield of isohexanes in *n*-hexane isomerization over Pt/HTsVM in the temperature range of 220–300 °C passes through a maximum at 260–270 °C and reaches 55.4–55.7 wt.%. The selectivity of isomerization at 220–260 °C is higher than 80% and drops with the temperature (Table 1, Fig. 3). At temperatures of >260 °C, the role of side reactions, *viz.*, cracking and disproportionation, that afford mainly saturated hydrocarbons C_3–C_5 significantly increases.

The modification of the TsVM zeolite-based Pt catalyst with Fe^{3+} cations results in inhibition of secondary processes and an increase in the selectivity of *n*-hexane isomerization over the whole temperature range studied (see Fig. 3). The maximum yield of isohexanes on Pt–Fe/HTsVM reaches 60.5 wt.% at a selectivity of

Table 1. *n*-Hexane isomerization on the modified zeolites TsVM and Beta (space velocity 1 h^{-1}, molar ratio H_2 : *n*-C_6H_{14} = 6 : 1)

Catalyst	*T*/°C	*X*[a]	*S*[b]	Yield (wt.%)						
		%		CH_4–C_4H_{10}	ΣC_5H_{12}	*iso*-C_6H_{14}				
						2,2-DMB[c]	2,3-DMB[d]	2-MP[e]	3-MP[f]	Σ*iso*-C_6H_{14}
0.5%Pt/HTsVM	240	49.9	88.0	4.4	1.6	Traces	1.0	32.4	10.5	43.9
	260	68.7	80.6	9.8	3.5	0.1	2.1	38.3	14.9	55.4
	270	74.8	74.5	14.8	4.3	0.1	2.2	37.6	15.8	55.7
0.5%Pt–1.5%Fe/HTsVM	240	37.9	93.7	1.7	0.7	0.1	25.9		9.5	35.5
	280	73.2	82.7	10.2	2.5	0.1	41.9		18.5	60.5
0.5%Pt–1.5%Ga/HTsVM	300	49.6	11.5	33.5	10.4	—	3.9		1.8	5.7
0.2%Pt/H-Beta[g]	250	82.1	96.0	2.5	0.8	12.9	9.0	34.8	22.1	78.8
0.5%Pt/H-Beta[g]	250	82.4	95.7	2.7	0.8	13.9	8.8	34.5	21.7	78.9

[a] *n*-Hexane conversion. [b] Selectivity to isohexanes.
[c] 2,2-Dimethylbutane. [d] 2,3-Dimethylbutane.
[e] 2-Methylpentane. [f] 3-Methylpentane. [g] Temperature of zeolite calcination is 500 °C.

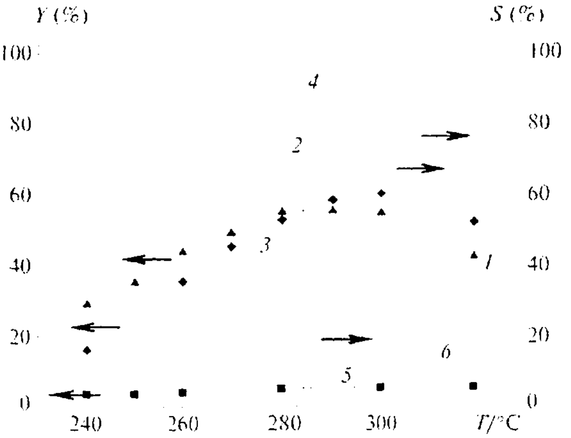

Fig. 3. The total yield (Y) of isohexanes (1, 3, 5) and selectivity (S) of their formation (2, 4, 6) as a function of the reaction temperature over the catalysts 0.5%Pt/HTsVM (1, 2), 0.5%Pt—1.5%Fe/HTsVM (3, 4), and 0.5%Pt—1.5%Ga/HTsVM (5, 6).

82.7%. Oppositely, the introduction of Ga^{3+} cations into Pt/HTsVM markedly decreases the catalytic activity. n-Hexane conversion on Pt—Ga/HTsVM at 230—300 °C is 17.8—49.6%, and hydrocracking and cracking of n-hexane to form C_1—C_5 hydrocarbons are the main reactions proceeding on this catalyst. The isohexane yield is at most 6 wt.%. The selectivity of n-hexane isomerization on Pt—Ga/HTsVM is 5—8 times lower than that on Pt/HTsVM. The low activity of the Pt—Ga/HTsVM catalyst in n-hexane isomerization can be due to localization of gallium cations on the zeolite external surface and hampered access of n-hexane molecules to the zeolite channels.[15]

The main products of n-hexane isomerization over all the catalysts based on zeolite HTsVM are 2- and 3-methylpentanes. Disubstituted isohexanes and 2,2- and 2,3-dimethylbutanes are virtually not formed over the TsVM zeolites. This is due to the features of the molecular-sieve properties of zeolite ZSM-5.[2,4,16] The pore size in ZSM-5 zeolite is 0.53×0.56 nm and 0.51×0.55 nm,[17] and this hampers the formation and diffusion of branched molecules in zeolite pores. Taking into account that the activities of Pt-containing catalysts based on zeolites HTsVM and H-Beta in n-pentane isomerization are close, one can conclude that the molecular-sieve effect becomes noticeable in the isomerization of normal alkanes containing more that five carbon atoms.

The catalysts based on the large-pore zeolite Beta are characterized by high activity and selectivity in n-hexane isomerization. The maximum yield of isohexanes over Pt/H-Beta is close to the equilibrium yield and is equal to 78.9 wt.% at a selectivity of 95.7% (see Table 1). The main products of n-hexane isomerization over the Pt catalysts based on zeolite Beta are 2- and 3-methylpentanes and 2,2- and 2,3-dimethylbutanes. Unlike pentasils, the yield of disubstituted isomers (2,2- and 2,3-dimethylbutanes) over Pt/H-Beta is one order of magnitude higher and close to 22 wt.%. A variation of the platinum concentration in the Pt/H-Beta catalyst from 0.2 to 0.5% virtually does not affect the yields of mono- and disubstituted hexanes.

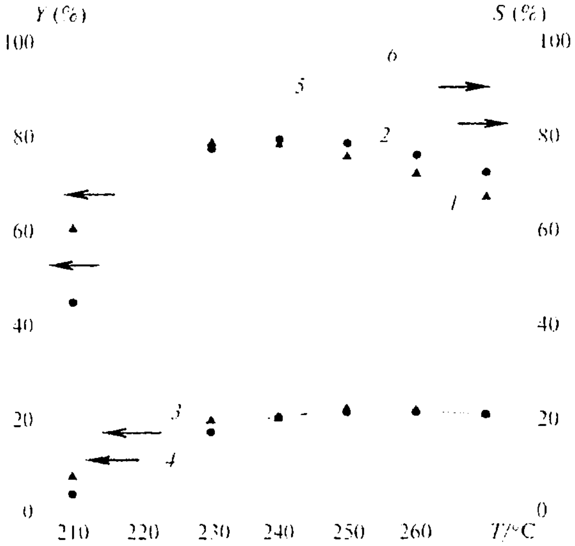

Fig. 4. The temperature effect on the yield (Y) of the sum of isohexanes (1, 2) and of disubstituted isohexanes (3, 4) and selectivity (S) in n-hexane (5, 6) on the Pt-containing catalysts based on the zeolite Beta thermally pretreated at various temperatures: 200 (1, 3, 5) and 500 °C (2, 4, 6).

The effect of the temperature of zeolite NH_4-Beta preliminary calcination on the catalytic properties in n-hexane isomerization is shown in Fig. 4. The properties of the catalysts based on zeolite Beta pretreated in a current of air at 200 °C and 500 °C are close. The maximum yield of isohexanes (78 wt.%) at a selectivity of 95—96% is observed at 230—240 °C.

The stability of the catalyst 0.2%Pt/H-Beta was tested under conditions providing the maximum yield of the

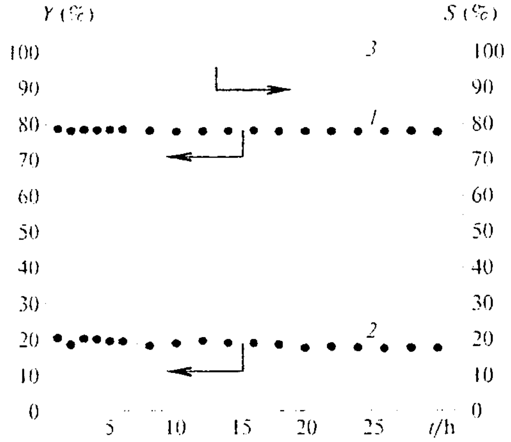

Fig. 5. Stability of the catalyst 0.2%Pt/H-Beta in n-hexane isomerization: the yield (Y) of the sum of isohexanes (1) and of disubstituted isohexanes (2) and selectivity (S) (3).

products of *n*-hexane isomerization (250 °C, space velocity of *n*-hexane 1 h^{-1}, molar ratio $H_2 : n\text{-}C_6H_{14} = 6 : 1$). The findings are presented in Fig. 5. The catalyst retained the activity and selectivity for 30 h of continuous operation. The total yield of isohexanes is 78.8—77.8 wt.% at a selectivity of 96.6—96.8%.

Thus, the Pt/H-Beta and Pt/HTsVM zeolites are the most efficient catalysts among the zeolite catalysts for *n*-pentane isomerization studied and the Pt systems based on zeolite Beta are most efficient for *n*-hexane isomerization. The catalyst 0.2%Pt/H-Beta is characterized by high activity, selectivity, and stability in *n*-hexane isomerization.

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