Effect of the nature of zeolite and modifying additives on the activity of zeolite-containing catalysts in *n*-butane isomerization

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Isomerization of *n*-butane on various types of zeolites (ZVM, ZVK, mordenite, and Y) modified with transition metals and cationic and anionic additives was investigated. Under the conditions studied, H-forms of zeolites are inactive. Pt-containing systems based on the H-form of ZVM (HZVM) are the most efficient catalysts for *n*-butane isomerization, and the yield of isobutane reaches 20—26 wt.% at a selectivity of 40—45%. Modification of this catalyst with Ga and Fe compounds or with an aqueous solution of HCl increases the selectivity with respect to isobutane up to 70—90%. Introduction of Zn^{2+} cations or F^- and SO_4^{2-} anions into the Pt-containing HZVM system decreases the selectivity and yield of isobutane due to the formation of very strong acidic centers on which disproportionation and hydrocracking of *n*-butane mainly occur.

Key words: zeolites, modified zeolites, *n*-butane, isobutane, isomerization.

The search for an efficient catalyst of skeletal isomerization of *n*-paraffins remains an urgent problem because isoparaffins are widely used for the preparation of high-octane components of gasoline and as additives for decreasing the freezing points of Diesel fuel. Available data on isomerization of *n*-paraffins on metal-zeolite catalysts deal mainly with hydrocarbons containing at least five C atoms,[1,2] whereas the isomerization of *n*-butane is much more poorly investigated.[3,4]

Very strong acidic sites are required for activation of molecules with a very short carbon chain, because the isomerization occurs, most likely, through the formation of carbenium ions.[5] It was mentioned[1,6,7] that *n*-alkane isomerization requires both Brönsted and Lewis acidic sites (BAS and LAS, respectively). Therefore, bifunctional zeolite catalysts combining strong acidic properties of zeolite with pronounced dehydrogenating properties of a supported metal are of interest.

In this work, we studied *n*-butane isomerization on different zeolites modified by transition metals and cationic and anionic additives at various temperatures, contact times, and hydrogen concentrations.

Experimental

Highly siliceous zeolites ZVM and ZVK with a SiO_2/Al_2O_3 molar ratio of 42 and 60, respectively, as well as mordenite (SiO_2/Al_2O_3 = 10) and zeolite Y (SiO_2/Al_2O_3 = 4.7) were used. Crystallinity of zeolites was determined on a DRON-3 diffractometer. It was 98—100% for highly siliceous zeolites (ZVM, ZVK), ~95% for mordenite and zeolite Y, and ~90% for dealuminated zeolites. In addition, HZVM—oxide (Al_2O_3, Al_2O_3—SiO_2, Al_2O_3—SiO_2—B_2O_3, MgO) compositions were used as supports. The zeolites and composites were modified by Pt, Pd, and Ru (0.5 wt.%); Ga^{3+}, Fe^{3+}, Cr^{3+}, and Zn^{2+} cations (1.5—2.0 wt.%); and Cl^-, F^-, and SO_4^{2-} anions (1.2—5.0 wt.%).

H-Forms of zeolites were prepared by triple ion exchange of Na^+ by NH_4^+ followed by the decomposition of the NH_4-form of zeolite in an air flow at 450—520 °C for 5 h. Some samples were heated in an air flow at 650—700 °C or subjected to thermal steam treatment. Pt-Zeolite catalysts were prepared under conditions of ion exchange of the NH_4-form of zeolite with $[Pt(NH_3)_4]Cl_2$. Other modifiers were introduced similarly or from aqueous solutions of the corresponding salts (nitrates, chlorides), or by the treatment of the H-form of zeolite with gaseous compounds (CF_3H, HCl) or aqueous solutions of H_2SO_4 or HCl.

Nonmodified zeolites were pre-calcined in an air flow at 450—500 °C. After calcination in air, catalysts modified by noble metals were reduced in a hydrogen flow at 350 °C for 1 h.

The reaction was carried out in a flow-type reactor at 320—400 °C and atmospheric pressure. The loading of the catalyst was 1 cm^3, the volume flow rate of *n*-butane was 300 h^{-1}, and the H_2 : n-C_4H_{10} molar ratio was varied from 0 to 8. The reaction products were analyzed by GLC on columns packed with Silipor 600 or Al_2O_3; the quantitative composition was calculated by the internal normalization method. The activity of catalysts was estimated from the yield of isobutane calculated from the passed *n*-butane.

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Results and Discussion

Under the conditions studied, cracking, disproportionation, and hydrocracking of *n*-butane and products of its transformation to form C_1—C_3 and C_5 hydrocarbons (Table 1) are the main reactions on H-forms of zeolites ZVM and mordenite. The yield of isobutane is only 2—4 wt.% at a selectivity of 10—40%. The high-temperature treatment of zeolite HZVM at 700 °C in an argon flow results in a substantial increase in the conversion of *n*-butane, although the yield of isobutane remains lower than 5 wt.%, and hydrocarbons C_2—C_3 are the main products. This can be explained by the formation of strong LAS due to dehydroxylation at 700 °C, which favors side reactions. Similar data have been obtained previously for cracking of *n*-hexane on high-silica zeolites.[8]

When platinum possessing dehydrogenating properties is introduced into zeolite, the yield of isobutane increases substantially (see Table 1). The highest yield (26.3 wt.%) was obtained on Pt/HZVM. The Pt catalysts based on HZVK, H-mordenite, and HY, as well as the Pt/HZVM system, which were preliminarily subjected to thermal or thermal steam treatment, exhibit a low activity. Selectivity of *n*-butane isomerization for the majority of Pt-zeolite catalysts is low and reaches 40—60% only in some cases.

To increase the yield of isobutane and selectivity of its formation, the Pt/HZVM catalyst was additionally modified by Ga^{3+}, Fe^{3+}, and Zn^{2+} cations or Cl^-, F^-, and SO_4^{2-} anions (Table 2). The introduction of Ga^{3+} or Fe^{3+} into the Pt-zeolite system increases the selectivity with respect to isobutane by 1.5 times (350 °C). Trivalent cations are not replaced by protons of the bridging OH groups in zeolite and do not change the number of BAS on which isomerization occurs.[9] Thus, these modifiers decrease the activity of Pt in hydrocracking reactions, increasing the selectivity of isomerization and the yield of isobutane. This agrees with the published data on the stabilizing effect of Ga on the dispersity and electron state of Pt in the zeolite systems.[10—12] The introduction of Zn^{2+} cations into the Pt-zeolite catalysts produces a negative effect. It is most likely that the replacement of protons of BAS by Zn^{2+} cations and the formation of strong LAS bound to the zinc ions[13,14] result in a noticeable decrease in the isobutane yield (see Table 2).

In order to vary the acidic properties of the catalyst, the highly siliceous zeolites HZVM and H-mordenite were modified by Cl^-, F^-, and SO_4^{2-} anions before the deposition of Pt. The treatment of zeolite with CF_3H *in vacuo* (200 °C, 1 h) results in a considerable dealumination of the zeolite lattice to form LAS[15] and a decrease in the selectivity with respect to isobutane. The modification of zeolite by SO_4^{2-} ions exerts a similar effect (see Table 2). A positive effect was observed after Cl^- ions were introduced from an aqueous solution of HCl into zeolite. The Pt/HZVM—Cl (1.2%) catalytic system obtained in this way is characterized by a high selectivity in *n*-butane isomerization (90%), and the yield

Table 1. Isomerization of *n*-butane on Pt-containing zeolites ($v_{C_4H_{10}}$ = 300 h^{-1}, molar ratio H_2 : *n*-C_4H_{10} = 4 : 1)[a]

Catalyst	*T*	*X*	$S_{i\text{-}C_4}$	Yield of products (wt.%)				
	/°C	(%)		CH_4	$C_2H_6/C_2^=$	$C_3H_8/C_3^=$	$C_5H_{12}+C_4^=$	*i*-C_4H_{10}
HZVM	350	6.5	19	0.1	0.9/Traces	4.3/Traces	Traces	1.2
	400	21.8	11	0.5	1.4/0.3	14.7/1.2	1.4	2.3
HZVM[b]	350	23.4	11	Traces	0.5/0.2	18.0/0.9	1.2	2.6
	400	43.4	10	0.7	2.2/1.0	32.1/1.9	1.2	4.3
H-Mordenite	350	9.7	26	0.1	0.1/Traces	6.5/—	0.5	2.5
	400	11.8	28	0.2	0.3/0.3	7.0/—	0.7	3.3
Pt/HZVM	350	41.1	45	3.6	8.4/—	10.6/—	—	18.5
	400	64.9	40	3.3	12.5/—	21.2/—	1.6	26.3
Pt/HZVK	350	58.0	24	7.5	16.5/—	20.0/—	—	14.0
	400	99.6	1	30.8	45.0/—	23.1/—	—	0.7
Pt/H-Mordenite	350	36.8	29	1.8	6.0/—	16.4/—	1.8	10.8
	400	43.0	27	3.4	8.7/—	17.5/—	1.6	11.8
Pt/HY	350	4.5	55	0.3	0.7/—	1.0/—	—	2.5
	400	16.9	65	1.0	1.8/—	3.1/—	—	11.0
Pt/HZVM[b]	350	1.8	100	—	—	—	—	1.8
	400	15.1	66	0.2	0.5/—	4.5/—	Traces	9.9
Pt/HZVM[c]	320	39.8	38	0.2	1.3/—	13.3/—	9.9	15.1
	350	70.5	23	0.4	5.9/—	36.7/—	11.0	16.5

[a] The following designations were used here and in Tables 2 and 3: *T* is temperature, *X* is conversion of *n*-butane, and $S_{i\text{-}C_4}$ is selectivity with respect to isobutane.

[b] HZVM was treated with air at 700 °C for 2 h.

[c] HZVM was dealuminated with steam.

Table 2. Influence of modifying additives on the activity and selectivity of the Pt-zeolite catalyst in *n*-butane isomerization ($v_{C_4H_{10}}$ = 300 h^{-1}, molar ratio H_2 : *n*-C_4H_{10} = 4 : 1)

Cata-lyst	*T* /°C	*X* (%)	S_{i-C_4} (%)	Yield of products (wt.%) CH_4	C_2H_6	C_3H_8	C_5H_{12}+$C_4^=$	*i*-C_4H_{10}
Pt/HZVM	350	41.1	45	3.6	8.4	10.6	—	18.5
	400	64.9	40	3.3	12.5	21.2	1.6	26.3
Pt,Ga/HZVM	350	32.7	73	0.5	0.8	4.8	2.8	23.8
	400	66.1	33	2.1	6.6	33.0	2.7	21.7
Pt,Fe/HZVM	320	13.7	74	0.3	0.9	1.7	0.7	10.1
	350	35.3	69	0.5	1.3	5.9	3.4	24.2
Pt,Zn/HZVM	350	23.7	45	0.1	0.8	6.7	5.4	10.7
	400	43.8	33	0.8	4.4	19.5	4.8	14.3
Pt/HZVM—Cl (1.2%)	350	20.3	90	0.1	0.3	1.2	0.5	18.2
	380	38.3	60	0.2	1.3	9.8	4.1	22.9
	400	43.5	41	0.4	3.6	17.4	4.2	17.9
Pt/HZVM—F	320	23.8	37	0.1	0.7	8.3	6.0	8.7
	350	53.2	26	0.3	3.6	26.5	9.2	13.6
Pt/HZVM—SO_4 (5%)	350	31.6	15	0.3	3.2	18.3	5.0	4.8
	380	50.3	12	0.7	7.8	32.0	3.9	5.9

Table 3. Influence of the catalyst composition on *n*-butane isomerization ($v_{C_4H_{10}}$ = 300 h^{-1}, molar ratio H_2 : *n*-C_4H_{10} = 4 : 1)

Cata-lyst	*T* /°C	*X* (%)	S_{i-C_4} (%)	Yield of products (wt.%) CH_4	C_2H_6	C_3H_8	C_5H_{12}/+$C_4^=$	*i*-C_4H_{10}
Pt/HZVM	350	41.1	45	3.6	8.4	10.6	—	18.5
	400	64.9	40	3.3	12.5	21.2	1.6	26.3
Pt/75% HZVM, 25% Al_2O_3	350	32.7	63	0.8	1.7	5.6	3.9	20.7
	380	59.8	50	1.3	2.9	14.8	10.9	29.9
Pt/50% HZVM, 35% Al_2O_3, 15% SiO_2	350	9.6	74	0.3	0.7	1.2	0.3	7.1
	400	30.8	74	0.9	1.4	4.5	1.2	22.8
Pt/70% HZVM, 30% Al_2O_3, 15% SiO_2, 5% B_2O_3	320	6.6	32	0.4	1.3	2.7	0.1	2.1
	350	12.8	48	0.7	1.7	4.1	0.2	6.1
Pt/70% HZVM, 30% MgO	320	3.2	97	—	—	0.1	—	3.1
	350	10.4	85	0.1	0.2	0.6	0.7	8.8
Pd/75% HZVM, 25% Al_2O_3	350	16.5	83	0.1	0.2	1.3	1.2	13.7
	380	30.0	54	0.2	0.8	6.9	6.0	16.1
Ru/75% HZVM, 25% Al_2O_3	320	20.0	13	4.2	8.5	4.7	—	2.6
	350	39.1	9	16.9	13.0	5.6	—	3.6
Pt,Cr/75% HZVM, 25% Al_2O_3	320	21.2	44	2.0	2.2	7.4	0.3	9.3
	350	46.3	49	3.4	4.6	13.8	2.0	22.5

of isobutane is 18.2 wt.%. (see Table 2). The treatment of zeolite with gaseous HCl is not so efficient as the modification by an aqueous solution.

The introduction of binders (Al_2O_3, Al_2O_3—SiO_2, Al_2O_3—SiO_2—B_2O_3, and MgO) into Pt/HZVM affects in different manners the activity and selectivity of the catalyst (Table 3). This is most likely due to different acidities of the composition components.

The catalysts modified by Pd and Ru are considerably less active in the isomerization of *n*-butane as compared to the Pt-containing systems (see Table 3).

The data obtained on the influence of the contact time (τ) and hydrogen concentration on the yield of isobutane and selectivity of isomerization in the presence of Pt,Ga/HZVM catalyst (Fig. 1) show that at 320 and 350 °C and the molar ratio H_2 : *n*-C_4H_{10} = 4 : 1, the conversion of *n*-butane and the yield of isobutane change insignificantly within the interval τ = 1.6—2.4 s but increase 1.5—2 times as τ further increases. The selectivity with respect to isobutane decreases. As the contact time increases to 4.8 s, cracking, hydrocracking, and disproportionation processes predominate, leading

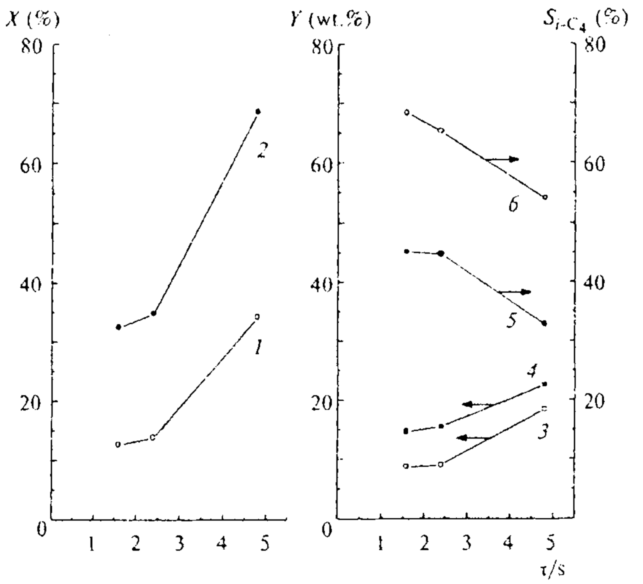

Fig. 1. Dependences of the conversion (X) of n-butane (*1, 2*), yield (Y) of isobutane (*3, 4*), and selectivity (S) with respect to isobutane (*5, 6*) on the contact time (τ) on Pt,Ga/HZVM at 320 °C (*1, 3, 5*) and 350 °C (*2, 4, 6*); molar ratio $H_2 : n\text{-}C_4H_{10} = 4 : 1$.

to the formation of C_1—C_3 and C_5 hydrocarbons, mainly propane, which results in a decrease in the selectivity with respect to isobutane.

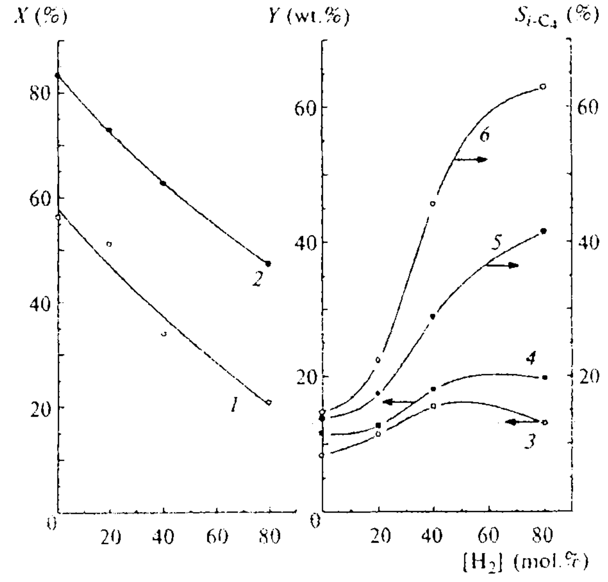

Fig. 2. Dependences of the conversion (X) of n-butane (*1, 2*), yield (Y) of isobutane (*3, 4*), and selectivity (S) with respect to isobutane (*5, 6*) on the concentration of H_2 in the reaction mixture ($n\text{-}C_4H_{10} + H_2 + He$) on Pt,Ga/HZVM at 320 °C (*1, 3, 5*) and 350 °C (*2, 4, 6*); τ = 2.4 s.

When the concentration of H_2 in the reaction mixture ($n\text{-}C_4H_{10} + H_2 + He$) increases, the conversion of n-butane decreases, and the selectivity with respect to isobutane increases by 3—4 times. The yield of isobutane passes through a maximum, which shifts toward higher H_2 concentrations as the temperature increases (Fig. 2). Therefore, an increase in the concentration of H_2 in the reaction mixture suppresses side processes, first of all, the formation of hydrocarbons C_2—C_3. The highest yield of isobutane is observed at H_2 concentration equal to 60—80 mol.%.

Thus, modification of Pt/HZVM catalysts by gallium, iron, and chlorine ions increases their selectivity in n-butane isomerization to 70—90%. When these modifiers are used, the yield of isobutane is 24 wt.%. The $H_2 : n\text{-}C_4H_{10}$ ratio exerts a substantial effect on the conversion of n-butane and selectivity of isomerization. When the concentration of H_2 in the reaction mixture increases to 80 mol.%, the conversion of n-butane decreases, and the selectivity with respect to isobutane increases by 3—4 times.

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