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Catalytic Activity of H-Forms of Zeolites in the Isomerization of Supercritical *n*-Pentane and Their Physicochemical Properties

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Abstract—The acidic properties of the H-forms of zeolites ZSM-5, Beta, Y, and mordenite are studied by diffuse reflectance IR spectroscopy using *n*-pentane as a probe molecule. The decreasing order of Brønsted acid site strengths is constructed. The isopentane selectivity in *n*-pentane isomerization under supercritical conditions (260°C, 130 atm) increases in the order H-ZSM-5 < H-Beta < H-mordenite(11) ≈ H-Y with decreasing strength of Brønsted sites. Catalytic data are analyzed jointly with the results of physicochemical studies of H-mordenite (temperature-programmed ammonia desorption, benzene adsorption, and IR spectroscopy). Under the supercritical conditions, the conversion of *n*-pentane on mordenite is determined by the total acidity of the zeolite and also by the accessibility of the acid sites inside the zeolite channels to the reactant.

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The production of isoalkanes is a challenging problem of present-day petroleum processing. Branched alkanes have high octane numbers and find use as components of gasoline. The main method of their preparation is the catalytic isomerization of *n*-alkanes.

The conversion of alkanes involves Brønsted acid sites (hydroxyl groups of zeolites) [1]. The activity of metal–zeolite catalysts and their isomerization selectivity are determined by the acidity and pore structure of the zeolite [2, 3]. Isomerization is carried out in the presence of hydrogen and platinum to suppress their deactivation due to secondary processes and the formation of condensation products (precursors of coke) on the catalyst surface. At present, performing the reaction in a hydrogen medium is considered to be the only possible way of achieving high stability and productivity of the process.

It was repeatedly shown in the latest decade that use of supercritical media in heterogeneous catalytic reactions also prevents the deactivation of solid-acid catalysts [4].

We demonstrated earlier [5, 6] that *n*-pentane isomerization under supercritical conditions affords an increase in the activity and operating stability of solid-acid catalysts along with enhancement of the isopentane selectivity as compared to the same reaction in the gas phase. We showed [6] that *n*-pentane in the supercritical state is efficiently isomerized on the H-forms of zeolites in the absence of supported platinum and hydrogen and that catalysts differ in activity under the same reaction conditions. We studied the physicochemical properties of zeolites to understand the causes of the difference between their catalytic effects in *n*-pentane isomerization under supercritical conditions. Thus, the purpose of the present work is to consider the acidic properties and physicochemical characteristics of the H-forms of zeolites jointly with the results of catalytic studies of *n*-pentane isomerization under supercritical conditions.

EXPERIMENTAL

Preparation of Catalysts

The H-forms of zeolites with the mordenite structure and Si/Al = 5 (H-mordenite(5)) and 11 (H-mordenite(11)), zeolite Beta (Si/Al = 38), ZSM-5 (Si/Al = 25), and zeolite Y (Si/Al = 2.5) were obtained by the thermal decomposition of their NH_4-forms. The initial powdered zeolites were pelletized and then crushed, and the 0.25–0.50 mm particle size fraction was taken. Next, the samples were calcined in a dry air flow at 500°C for 3 h.

The H-mordenite samples with Si/Al = 20 and 36 were prepared by dealumination [7]. The initial H-form of mordenite (Si/Al = 6.4) was converted into the NH_4-form by ion exchange in an aqueous solution of ammonium nitrite. The NH_4-form of mordenite was calcined in a muffle furnace at 640°C for 4 h. The resulting H-form of mordenite was treated with an aqueous solution of hydrochloric acid. To prepare H-mordenite with different Si/Al ratios, 2 and 6 N HCl was used. Thereafter, the dried powder was pressed and crushed, and the 0.25–0.50 mm particle size fraction was taken. The samples were then calcined in a dry air flow at 500°C for 3 h.

Catalytic Experiments and Analysis of the Reaction Products

n-Pentane was isomerized under supercritical conditions at 260°C and 130 atm in the absence of hydrogen or additional solvents in a laboratory-scale flow reactor. The pressure in the system was created by *n*-pentane supply using a high-pressure piston liquid pump and was controlled using a membrane valve. The LHSV of the substrate (V_l, cm^3/(h cm^3 Cat)), defined as the ratio of the flow rate of the reactant in the liquid state at 20°C to the catalyst volume (0.2 cm^3), was 30 h^{-1}. Heating the system to the reaction temperature was carried out in a hydrocarbon flow at the preset pressure.

The reaction products were analyzed by GLC using a capillary column (100 m) packed with the OV-101 phase with online sampling. The quantitative composition of the conversion products was determined by the internal normalization method. The conversion of the initial *n*-alkane and the *i*th reaction product selectivity were calculated using the formulas

$$K = (c_{\rm in} - c_{\rm fin})/c_{\rm in} \times 100\%$$

and

$$S_i = (c_{{\rm fin},\,i} - c_{{\rm in},\,i})/(c_{\rm in} - c_{\rm fin}) \times 100\%,$$

respectively, where $c_{\rm in}$ and $c_{\rm fin}$ are the initial and final concentrations of *n*-pentane and $c_{{\rm in},\,i}$ and $c_{{\rm fin},\,i}$ are the weight concentrations of component *i* in the initial hydrocarbon and in the reaction products.

The catalytic experiments under supercritical conditions were described in greater detail in a previous publication [5].

IR Spectroscopy

The acidic properties of the H-forms of the zeolites mordenite, Beta, Y, and ZSM-5 were studied by diffuse reflectance IR spectroscopy using *n*-pentane as the probe molecule. IR spectra were recorded using a thin-wall quartz tube with a glued-in CaF$_2$ window. Before IR measurements, the samples were activated using a glass vacuum setup. The residual pressure under pumping was 10^{-4} Torr. The presynthesized H-form of a zeolite was heated in vacuo at 100°C for 1 h, then the temperature was slowly increased to 450°C, and the sample was pumped for 2 h. *n*-Pentane adsorption of was carried out at room temperature.

IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer with a diffuse reflectance attachment at room temperature in the 6000–2000 cm^{-1} range with 4-cm^{-1} resolution. The spectra were converted to the Kubelka–Munk units using the OMNIC program under the assumption that the reflectance of the zeolite at 5000 cm^{-1} is 0.9. Overlapped absorption bands were decomposed into their components under the assumption that separate bands are Gaussian-shapes. Computer processing also included spectrum smoothening and the subtraction of the background.

Physicochemical Studies of H-Mordenite Samples

The amount of acid sites was determined by the temperature-programmed desorption of ammonia (NH$_3$ TPD). Measurements were performed on a semiautomated setup using a calibrated IR spectrometer as the NH$_3$ detector. Before measurements, the catalyst was blown with N$_2$ at 500°C for 1 h. Ammonia was adsorbed at room temperature (5% NH$_3$ in N$_2$). The amount of adsorbed ammonia was measured under linear heating of the sample in a nitrogen flow in the temperature range from 100 to 600°C.

The degree of crystallinity and the modulus of mordenite samples were determined by X-ray diffraction on a DRON-2 diffractometer (CuK_α radiation, goniometer angular velocity of 2 deg/min, $2\theta = 15°$–$30°$). CeO$_2$ powder was used as the internal standard, whose amount was 10% of the zeolite weight.

The adsorption of benzene vapor on H-mordenite(5) and H-mordenite(11) was studied uisng a gravimetric adsorption setup equipped with a McBain balance. Before measurements, the samples were pumped at 400°C to constant weight. The residual pressure was 10^{-4} Torr. Benzene adsorption was measured at room temperature.

RESULTS AND DISCUSSION

Conversion of n-Pentane on the H-Forms of Zeolites

The critical parameters of *n*-pentane are 196.6°C and 33.3 atm, and those of isopentane are 187.4°C and 33.4 atm. Thus, at temperatures above 200°C and pressures higher than 40 atm, the reaction system is in the supercritical state at any conversion of *n*-pentane.

The results of *n*-pentane isomerization under the supercritical conditions on the H-forms of zeolites at 260°C and 130 atm are given in Table 1. These results show that the H-form of mordenite (Si/Al = 11) is the most active unpromoted zeolite catalyst, and zeolite Y is the least active. Sixty minutes after the catalyst was heated to the reaction temperature, the conversion of *n*-pentane on H-mordenite(11) is 30% at 87% isopentane selectivity. Along with isopentane, C$_3$, C$_4$, and C$_{6+}$ hydrocarbons resulted from the process, indicating that secondary disproportionation, oligomerization, and cracking reactions occur, but to a lesser extent than on the other zeolites. It is noteworthy that the conversions of *n*-pentane on H-mordenite(5) and H-mordenite(11) differ by one order of magnitude. In the series of mordenites with Si/Al = 6.5, 20, and 36, the conversion decreases with an increase in the degree of dealumination. There is a substantial difference between H-mordenite(11) and H-ZSM-5 in activity and selectivity in *n*-pentane conversion. As follows from the data presented, the isopentane selectivity of pentasil ZSM-5 is only 30% at 5% conversion. Light hydrocarbons, C$_3$ and C$_4$, forming with 47% selectivity, dominate the reaction product.

Table 1. Isomerization of *n*-pentane on the H-forms of zeolites under supercritical conditions (260°C, 130 atm, $V_1 = 30$ h^{-1}, reaction time of 60 min)

Catalyst	Si/Al	Conversion, %	Selectivity, wt %		
			C_3–C_4	*iso*-C_5	C_{6+}
H-mordenite(11)	11	30.0	6.6	87.4	6.0
H-mordenite(6.4)	6.4	17.2	6.7	88.3	5.0
H-mordenite(20)	20*	11.5	11.7	80.1	8.2
H-mordenite(36)	36*	5.5	8.9	83.9	7.2
H-mordenite(5)	5	2.7	23.8	70.4	5.8
H-ZSM-5	25	4.7	46.8	29.9	23.3
H-Beta	38	1.1	17.2	70.9	11.9
H-Y	2.5	0.3	9.6	87.1	3.3

* According to the X-ray diffraction data.

In spite of its high isopentane selectivity, zeolite Y is very inactive: under the conditions examined, the *n*-pentane conversion was as low as 0.3%.

Brønsted acid sites play the key role in *n*-alkane isomerization on zeolite catalysts under conventional gas-phase conditions [8]. Therefore, it seemed promising to correlate the acidic properties of the H-forms of zeolites with the results of catalytic studies of *n*-pentane isomerization under the supercritical conditions.

IR Spectroscopic Study of the Acidity of Zeolites

Three groups of absorption bands can be distinguished in the IR spectra of the H-forms of the zeolites (Figs. 1–4) in the region of the stretching vibrations of OH groups, namely, the bands due to the silanol Si–OH groups, the OH groups at aluminum ions, and bridging hydroxyl groups Si(OH)Al.

The positions of the absorption bands of the OH groups in the initial IR spectra of the zeolites coincide

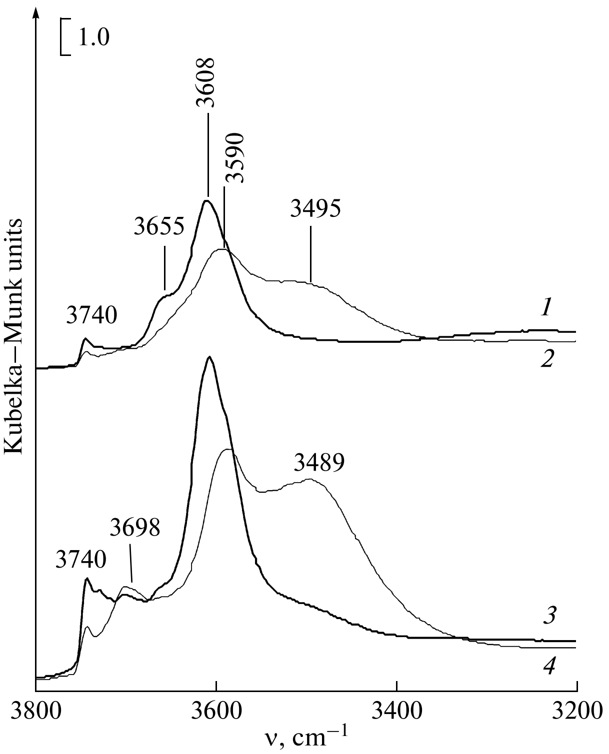

Fig. 1. IR spectra of the OH groups of H-mordenite (*1*, *3*) before and (*2*, *4*) after the adsorption of *n*-pentane (15 Torr): (*1*, *2*) H-mordenite(5) and (*3*, *4*) H-mordenite(11).

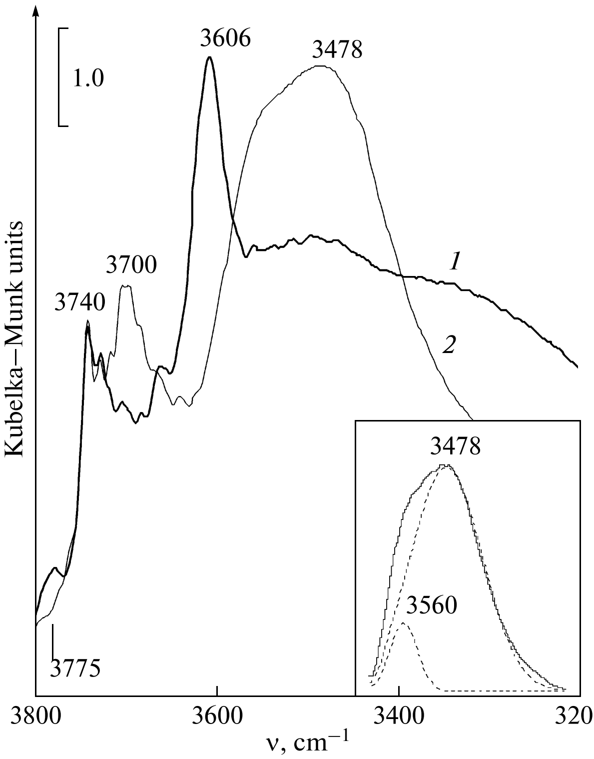

Fig. 2. IR spectra of the OH groups of H-Beta (*1*) before and (*2*) after the adsorption of *n*-pentane (15 Torr).

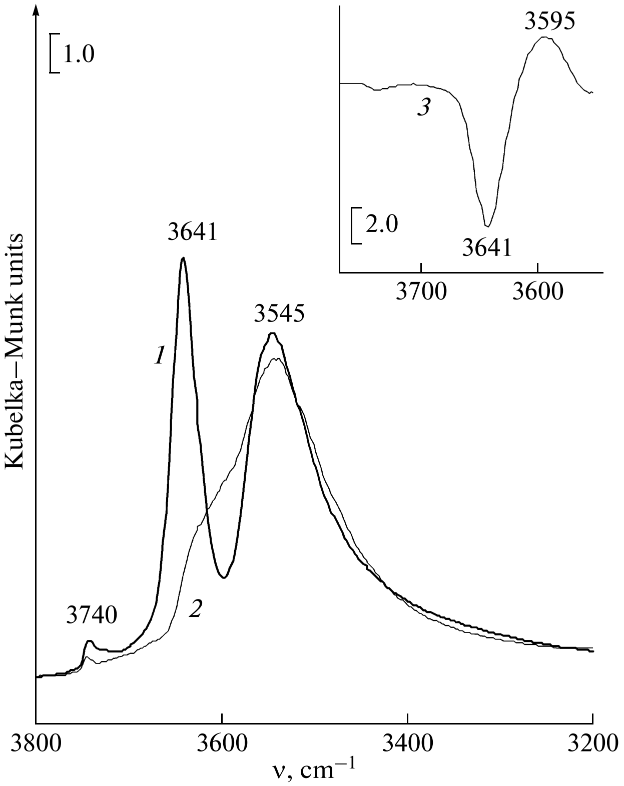

Fig. 3. IR spectra of the OH groups of H-Y (*1*) before and (*2*) after the adsorption of *n*-pentane (15 Torr); (*3*) differential spectrum obtained by subtraction of initial spectrum *1* from spectrum *2*.

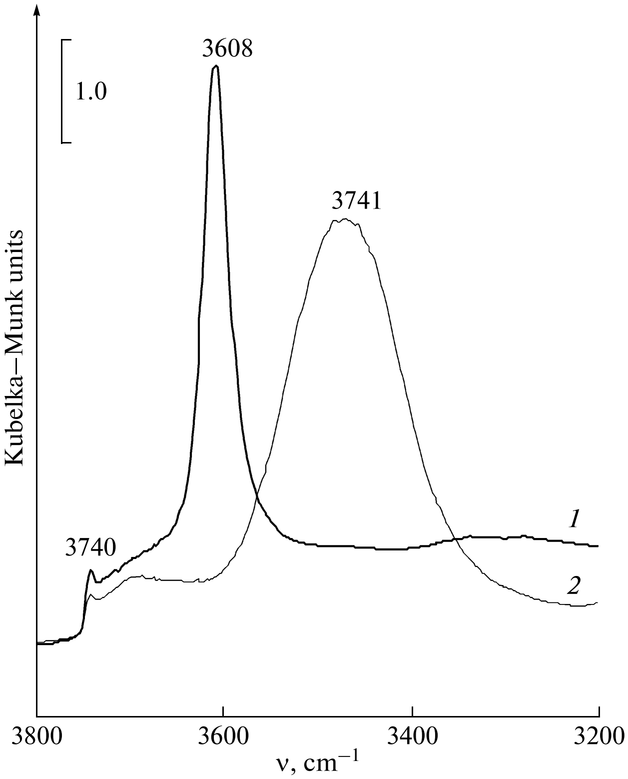

Fig. 4. IR spectra of the OH groups of H-ZSM-5 (*1*) before and (*2*) after the adsorption of *n*-pentane (15 Torr).

with the published data [9–12] within ±1–2 cm^{-1}. The narrow absorption band at 3740 cm^{-1}, observed in the spectra of all zeolites, is due to the terminal silanol groups. The most intense absorption band at 3608–3606 cm^{-1} is due to bridging Si(OH)Al groups. The broad band in the spectrum of zeolite H-Beta (Fig. 3) in the 3550–3200 cm^{-1} region pertains to hydrogen-bonded OH groups [10]. The absorption bands at 3641 and 3545 cm^{-1} in the initial spectrum of H–Y (Fig. 4) are due to the bridging OH groups located in large zeolite cavities and sodalite cages, respectively [11]. According to published data [10], the weak absorption band at 3655 cm^{-1} in the spectrum of H-mordenite(5) corresponds to the OH groups at extraframework aluminum ions (Fig. 1, spectrum *1*).

The interaction of *n*-pentane with the H-forms of zeolites substantially changes their spectra in the region of OH group vibrations. After *n*-pentane was in contact with H-mordenite, the intensity of the absorption band at 3608–3606 cm^{-1} is lower and a broad band appears in the low-frequency region, with a maximum at 3490–3500 cm^{-1} (Fig. 1). This indicates that there is interaction between the hydroxyl groups and pentane. The intensity of the initial band decreases only by one-third relative to its initial value, and its maximum shifts insignificantly from 3608 to 3590 cm^{-1}. The absorption band at 3608 cm^{-1} consists of two overlapped bands at 3612 and 3590 cm^{-1} due to the stretching vibrations of the bridging OH groups localized in large channels and small cavities (so-called “side pockets”) in the mordenite structure [12]. The channels have considerably larger sizes of the inlet window than the side pockets: 6.5 × 7.0 Å versus 2.6 × 5.7 Å [13]. Since the kinetic diameter of the *n*-pentane molecule is 4.3 Å [14], it is evident that *n*-pentane can penetrate only into large channels. The bridging hydroxyl groups located in the side pockets are inaccessible to *n*-pentane. This is confirmed by the spectroscopic data presented in Fig. 1. After pentane adsorption, the band of the Si(OH)Al groups (3612 cm^{-1}) located in larger channels of mordenites is shifted to lower frequencies by about 120 cm^{-1}. Due to this, the band of the OH groups located in the side pockets appears as an individual absorption band at 3590 cm^{-1}. Thus, only part of the Si(OH)Al acid sites of mordenite is accessible to *n*-pentane.

The small, but reliably detectable, difference (6 cm^{-1}) between the positions of the shifted absorption band of the Si(OH)Al groups in the mordenite samples with Si/Al = 5 and 11 is likely due to the fact that the proportion of $(SiO)_3Si–OH-Al(OSi)_3$ groups, which are more acidic than $(SiO)_2(AlO)–OH–Al(OSi)_3$, increases with an increase in the Si/Al ratio.

Table 2. Shift of absorption bands of the bridging Si(OH)Al groups in the IR spectra of the H-forms of zeolites after *n*-pentane adsorption

Zeolite	ν(Si(OH)Al), cm^{-1}	ΔνOH, cm^{-1}
H-ZSM-5	3608	137
H-Beta	3606	128
	3550–3200	46
H-mordenite(11)	3606	123
	(3612, 3590)	
H-mordenite(5)	3608	117
	(3612, 3590)	
H–Y	3641	46
	3545	–

Zeolite Beta also contains Si(OH)Al groups of two types, although in the initial spectrum (Fig. 2) they are represented by a single band at 3606 cm^{-1} [10]. The IR spectroscopic separation of these groups is possible only after their contact with a weak base, such as *n*-pentane. The asymmetric shape of the new broad band at 3600–3400 cm^{-1} indicates that this band consists of several unresolved components. The decomposition of this band into the components makes it possible to distinguish two peaks at 3560 and 3480 cm^{-1}. The shift of their maximum relative to the initial position is 46 and 126 cm^{-1}, respectively, which indicates different acidities of the bridging hydroxyl groups. However, all Si(OH)Al groups of zeolite Beta, unlike those of mordenite, are accessible to pentane.

The shift of the Si(OH)Al band of zeolite Y can be determined only from the differential spectrum [9]. The subtraction of initial spectrum *1* from spectrum *2* demonstrates that the absorption band at 3641 cm^{-1} is shifted to 3595 cm^{-1} (Fig. 3). The size of the inlet window of a sodalite cage in zeolite Y is smaller than the kinetic diameter of the *n*-pentane molecule, and, hence, the hydroxyl groups located in the sodalite cages are inaccessible to *n*-pentane, and this is the reason why the position of the low-frequency band at 3547 cm^{-1} remains unchanged.

Since the size of the inlet window of the channels in zeolite ZSM-5 (5.6 × 5.3 Å [14]) is sufficiently large for *n*-pentane molecules to penetrate, the absorption band at 3608 cm^{-1} disappears completely after adsorption, and a broad band at 3470 cm^{-1} (Fig. 4) appears, which is due to the interaction of *n*-pentane with Si(OH)Al groups.

Thus, it was shown by IR spectroscopy that *n*-pentane interacts with the OH groups of mordenite and zeolites Beta, ZSM-5, and Y. The value of the shift of the absorption band maximum of the OH groups (ΔνOH) characterizes the strength of interaction of the OH groups with *n*-pentane [15].

Based on the data obtained (Table 2), the following decreasing order of Brønsted acid site strengths can be constructed for the H-forms of the zeolites using the shift of the vibration frequency of the bridging Si(OH)Al groups upon *n*-pentane adsorption as the criterion:

$$\text{H-ZSM-5} > \text{H-Beta} > \text{H-mordenite(11)} > \text{H-mordenite(5)} \gg \text{H–Y}.$$

This order of acid site strengths correlates with IR spectroscopic data for probe molecules of different natures [9, 16]. The advantage of *n*-pentane as the probe molecule is that *n*-pentane is also a substrate of the isomerization reaction examined.

A simultaneous analysis of the IR spectroscopic data and the above catalytic data suggests that the increasing order of the isopentane selectivities of zeolites in *n*-pentane isomerization under the supercritical conditions,

$$\text{H-ZSM-5} < \text{H-Beta} < \text{H-mordenite(11)} \approx \text{H–Y}$$

coincides with the increasing order of Brønsted acid site strengths for the H-forms of the zeolites.

Influence of the Composition of the Mordenite Framework on the Catalytic Activity and Acidic Properties

As can be seen from the data in Table 1, the catalytic activities of the mordenites differ substantially. The *n*-pentane conversions on the Si/Al = 5 and 11 H-mordenites differ by one order of magnitude. For this reason, H-mordenite(5) and H-mordenit(11) were studied in greater detail using physicochemical methods.

The amount of acid sites in these samples was determined by temperature-programmed ammonia desorption. The NH_3 TPD spectra of the mordenites consist of two peaks, namely, a low-temperature peak at 190–210°C and a high-temperature peak at ~500°C. According to the literature [17], only the high-temperature peak is due to ammonia desorption from strong Brønsted acid sites. Although the H-mordenite samples have equal amounts of such sites (Fig. 5), their catalytic activities differ considerably. Since the kinetic diameters of the ammonia and *n*-pentane molecules differ substantially (2.6 and 4.3 Å, respectively [14]), it can be assumed that not all of the sites adsorbing ammonia can interact with *n*-pentane. For this reason, we studied the accessibility of the acid sites by benzene adsorption (the kinetic diameter of the benzene molecule is 4.9 Å [14]). As can be seen from Fig. 6, H-mordenite(5) adsorbs a smaller amount of benzene, while both samples have similar amounts of Brønsted acid sites, according to the NH_3 TPD data. It is most likely that these results are explained by the partial decomposition of the zeolite structure. According to X-ray diffraction data, the degree of crystallinity of heat-treated H-mordenite(5) is 80%, whereas that of heat-treated H-mordenite(11)

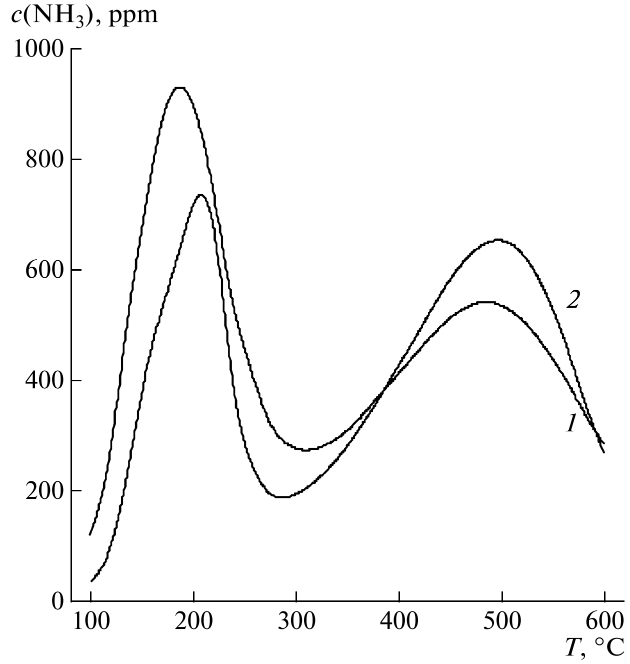

Fig. 5. Temperature-programmed ammonia desorption spectra of mordenites: (*1*) H-mordenite(5), C_{NH_3} = 2.13 mmol/g, $C_{NH_3, 300–600°C}$ = 1.11 mmol/g; (*2*) H-mordenite(11), C_{NH_3} = 1.71 mmol/g, $C_{NH_3, 300–600°C}$ = 1.10 mmol/g (C_{NH_3} is the amount of desorbed ammonia).

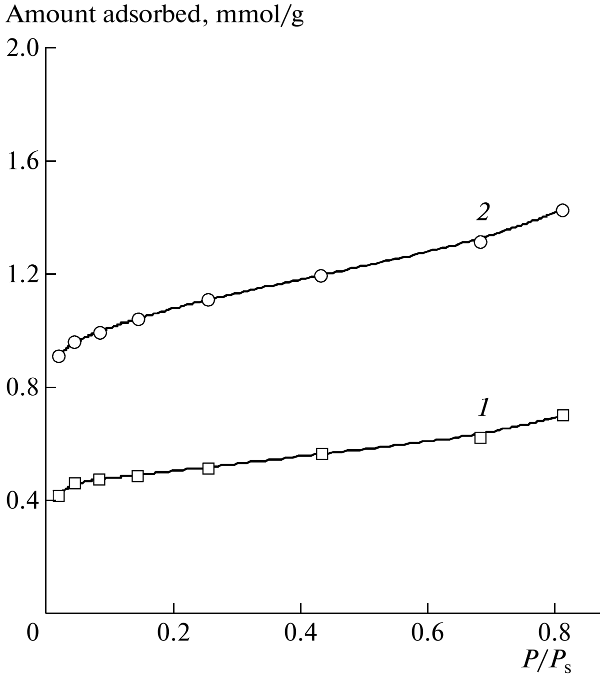

Fig. 6. Adsorption of benzene: (*1*) H-mordenite(5) and (*2*) H-mordenite(11).

is 95%. (The starting NH_4-forms of the zeolites had 100% crystallinity.) Thus, the partial decomposition of the structure and channel blocking occur during the preparation of the H-mordenite(5) catalyst. This is confirmed by the presence of the absorption band corresponding to the extraframework Al–OH groups only in the spectrum of H-mordenite(5) (Fig. 1, 3655 cm^{-1}). The presence of extraframework fragments in one-dimensional channels of mordenite considerably limits the adsorption of large molecules [18].

A comparison between the results of the catalytic and physicochemical studies shows that *n*-pentane isomerization involves the acid sites localized in the zeolite channels. The difference between the activities of H-mordenite(5) and H-mordenite(11) is due to the different accessibilities of these sites to *n*-pentane. Mordenites obtained from different sources can substantially differ in activity, which is explained both by the different numbers and strengths of their Brønsted acid sites and by the different accessibilities of the zeolite channels to the diffusion of *n*-pentane molecules. At the same time, the activity of mordenite should increase with an increase in the Si/Al ratio within a given sample series, which is primarily due to a decrease in the number of Brønsted active sites. This is confirmed by the results of *n*-pentane isomerization on the Si/Al = 6.4, 20, and 36 H-mordenites (Table 1). The starting H-mordenite(6.4) possesses the highest activity, and the conversion of *n*-pentane on the dealuminated samples is lower and decreases with an increase in the degree of dealumination.

Thus, we established a correlation between the isopentane selectivity of the H-forms zeolites in *n*-pentane isomerization under supercritical conditions and the strength of their Brønsted acid sites. At the same time, it was found that the most selective catalyst, H-mordenite, has weaker acid sites than zeolites Beta and ZSM-5. The conversion of *n*-pentane under supercritical conditions is determined by the total acidity of the zeolite and also by the accessibility of its acid sites to alkane molecules, as was demonstrated for a series of dealuminated mordenites with different Si/Al ratios.

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