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IR Spectroscopic Study of Alkane Interaction with the Brønsted Acid Sites of Hydrogen-Exchanged Zeolites

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Abstract—Diffuse-reflectance IR spectroscopy is used to study the interaction of C_3 and C_6 alkanes (propane, *n*-hexane, 3-methylpentane, and cyclohexane) with the Brønsted acid sites of hydrogen-exchanged mordenite, ferrierite, ZSM-5, and faujasite. It is found that a shift of the absorption band of the stretching vibrations of acidic Si(OH)Al groups toward lower frequencies ($\Delta\nu$OH) due to the formation of a hydrogen bond with adsorbed alkanes increases in the following series: $\Delta\nu$OH(propane) < $\Delta\nu$OH(*n*-hexane) = $\Delta\nu$OH(3-methylpentane). The accessibility of Si(OH)Al groups to alkane molecules is determined by the dimension of rings through which molecules enter zeolite channels and cavities. It follows from the measured $\Delta\nu$OH values that the strength of Brønsted acid sites decreases in the following series: HZSM-5 > H-mordenite ≈ H-ferrierite ≫ HY. The difference between the three high-silica zeolites is not great. The results obtained are compared with the published IR data on Si(OH)Al groups of zeolites with adsorbed alkanes and other weak bases.

INTRODUCTION

Zeolite catalysts are widely used in the petrochemical industry in the process of hydrocarbon conversions such as cracking, hydrocracking, isomerization, and others. This group of reactions belongs to the processes of acid–base type occurring with the participation of Brønsted acid sites (the hydroxy groups of zeolites). Therefore, considerable attention has been given to the study of Brønsted acid sites in hydrogen-exchanged zeolites.

IR spectroscopy of probe molecules, which are weak bases that form hydrogen bonds with the OH groups of zeolites, has been successfully used for a long time in the studies of Brønsted acid sites (see, for instance, [1]). This method provides molecular-level information on the strength of acid sites in zeolites, their distribution over different sites in zeolites, and their accessibility to molecules with different geometries and shapes (shape selectivity). Various weak bases were used as probe molecules for Brønsted acid sites: H_2 [2–4], N_2 [2, 4, 5], CO [2, 4], NO [4], Ar and O_2 [2], and hydrocarbons (alkanes, alkenes, and arenes) [6–11]. In our opinion, the study of acid sites of zeolites based on probing their interactions with alkanes is preferable because alkanes are the substrates of several catalytic reactions of the acid–base type. However, very few papers have been published along these lines. The adsorption of normal and isostructured C_3–C_6 alkanes on H-mordenite, HY, and HZSM-5 was studied by *in situ* IR spectroscopy, calorimetry, and gravimetry [9]. The adsorption of various hydrocarbons (alkanes, alkenes, and aromatic hydrocarbons) on HZSM-5 was studied in [10, 11]. Zholobenko, Lukyanov, *et al.* [7, 8] compared the properties of acid sites in the zeolites with similar structures: H-ferrierite and SUZ-4. Analysis of literature known to us shows that data of different authors on the shifts of OH group stretching vibrations in alkane adsorption and the strengths of Brønsted acid sites related to these shifts in H-zeolites do not always agree even at a qualitative level.

In connection with this, the goal of this work was to analyze the trends in the shifts of stretching vibrations of Brønsted acid sites in hydrogen-exchanged high-silica zeolites (mordenite, ferrierite, and ZSM-5), and in faujasite HY depending on the nature and geometry of adsorbed C_3 and C_6 alkanes. We tried to systematize the results obtained in our study taking into account published data and to classify Brønsted acid sites in the zeolites according to their strength.

EXPERIMENTAL

In this work, we studied the following hydrogen-exchanged zeolites: H-mordenite (HM) with a Si/Al ratio of 5 (HM(5)) and 15 (HM(15)), H-ferrierite (HFer) with Si/Al = 10, HY with Si/Al = 2.4, and HZSM-5 with Si/Al = 15. Hydrogen-exchanged zeolites were obtained from the corresponding ammonium-exchanged zeolites, which were prepared using standard double ion-exchange procedure with 1 mol/l NH_4NO_3 solution. Before recording IR spectra, zeolite samples were loaded in a quartz ampule with a side arm and a CaF_2 window and subjected to thermal vacuum treatment according to the following scheme. First, the sample was treated in a vacuum (~10^{-4} torr) at 100°C for 2 h, and then the temperature was slowly increased (for 3 h) to 450°C. Then, the sample was allowed to stay under continuous evacuation at this temperature for 3 h.

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Propane from a cylinder was purified in a vacuum system to remove the traces of air and water by freezing it out into a trap cooled with liquid nitrogen, evacuating to ~10^{-3} torr, and further withdrawing the middle fraction from unfreezing solid propane. *n*-Hexane, 3-methylpentane (Fluka) and cyclohexane (Fluka) were purified using the same technique. Alkane adsorption on zeolites was carried out at room temperature and 60–65 torr (propane) or 10 torr (C_6 alkanes).

Diffuse-reflectance IR spectra were recorded at room temperature using a Nicolet Impact 410 Fourier-transform IR spectrometer equipped with an attachment for measuring the diffuse-reflectance spectra at 2000–6500 cm^{-1}. The resulting spectra were transformed into the Kubelka–Munk units assuming that the reflecting ability of a zeolite at 5000 cm^{-1} was 0.9.

RESULTS

Alkane Adsorption on H-Mordenites

In the IR spectrum of HM(5) in the region of OH group stretching vibrations (Fig. 1, spectrum *1* and Table 1), we observed three absorption bands at 3740, 3653, and 3606 cm^{-1}. According to [6], the most intense band at 3606 cm^{-1} is a combination of two superimposing bands at 3612 and 3590 cm^{-1}, which were assigned to the stretching vibrations of bridging OH groups of Si(OH)Al localized in large channels and in the so-called side pockets (small cavities), respectively, in the structure of HM. The band at 3653 cm^{-1} most likely refers to OH groups localized at the extraframework Al ions, which are present in small amounts in the initial zeolite. A narrow band at 3740 cm^{-1} belongs to the terminal silanol groups. The latter band has a shoulder at 3728 cm^{-1}, which points to the complex structure of this band. Trombetta *et al*. [10, 11] proposed that the band at 3740 cm^{-1} consists of two close bands of ≡Si(OH) groups localized on the outer surface of the zeolite and in zeolite channels.

The IR spectra of the initial HM(15) with a lower concentration of aluminum (Si/Al = 15) are analogous to the spectra of HM(5) (Table 1). Note, however, that the relative intensity of the absorption bands at 3740 cm^{-1} in HM(15) is several times higher than in HM(5) (Fig. 2, spectrum *1*).

After the contact of alkanes with zeolites HM at room temperature, substantial changes are observed in the IR spectra of OH groups. These changes are due to the formation of hydrogen bonds with alkanes (Fig. 1, Table 1). The maximum at 3606 cm^{-1} shifts to 3590 cm^{-1} and a broad band appears at 3500 cm^{-1}. The shift of this band (ΔνOH) from 3605 cm^{-1} is within 100–125 cm^{-1} and increases in the following series: propane < cyclohexane < *n*-hexane ≈ 3-methylpentane (Table 1). The Breck kinetic diameter [12] of studied alkane molecules is 4.3 Å for propane and *n*-hexane, 5.0 Å for 3-methylpentane, and 6.0 Å for cyclohexane. Therefore, it is clear that these molecules can only penetrate into large channels of HM with entrance windows of 6.5 × 7(Å) and cannot react with the Si(OH)Al groups in the side pockets with entrance windows of 2.6 × 5.7 Å [13]. Thus, C_3 and C_6 alkane adsorption on HM leads to a shift of the band of bridging Si(OH)Al groups in large channels (3612 cm^{-1}) toward lower frequencies. As a result, the band of Si(OH)Al groups localized in side pockets manifests itself as a single band at 3590 cm^{-1}.

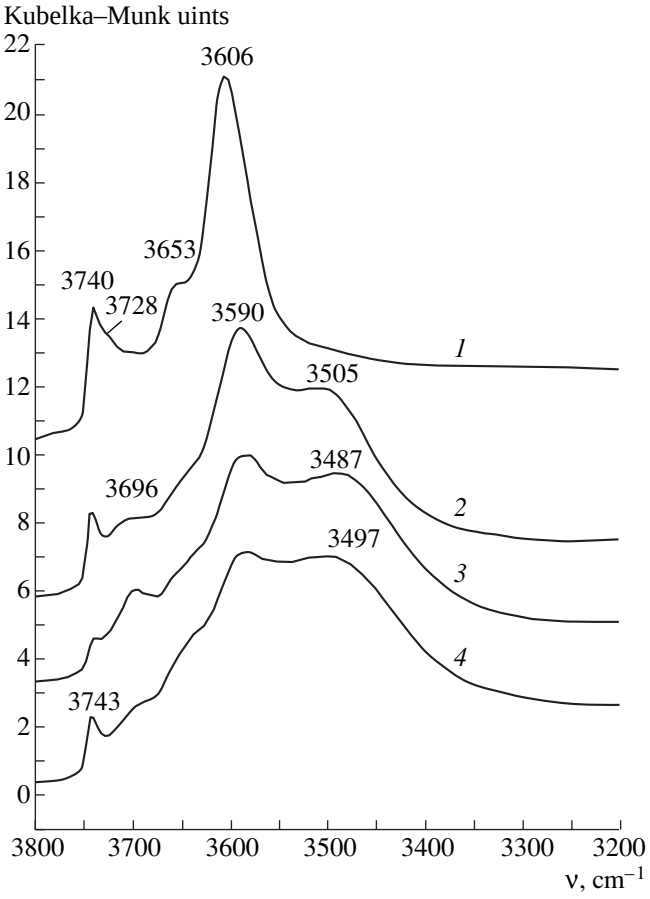

Fig. 1. IR spectra of H-mordenite (Si/Al = 5): (*1*) initial, (*2*) after propane adsorption, (*3*) after *n*-hexane adsorption, (*4*) and after cyclohexane adsorption at room temperature.

It is generally assumed that the value of the frequency shift of the stretching vibrations of acidic OH groups $\Delta\nu^{OH}$ due to their interactions with weak bases characterizes the strength of a hydrogen bond: the higher the value of $\Delta\nu^{OH}$, the stronger the interaction [14]. It follows from this principle that propane interacts with Si(OH)Al more weakly than C_6 alkanes. This agrees with the data of Eder *et al*. [9], who found that $\Delta\nu^{OH}$ monotonically increases with an increase in the number of carbon atoms from three to six in normal alkanes adsorbed on HZSM-5, HM, and HY. The small, but reliably detected, difference in ΔνOH for *n*-hexane and cyclohexane (Table 1) is probably due to the difference in the geometry of these molecules and the existence of cyclohexane conformers. This assumption

Table 1. Position of OH group bands (cm^{-1}) in hydrogen-exchanged zeolites before and after alkane adsorption

Adsorbate	Si(OH)		Al(OH)	Si(OH)Al		Δν
	H-mordenite (Si/Al = 5)					
Initial	3740**	3728	3653	3606		
Propane		3696		3590	3505	101
n-Hexane		3696		3590	3487	119
Cyclohexane		3696		3590	3497	109
	H-mordenite (Si/Al = 15)					
Initial	3740**	Shoulder	3658	3606		
n-Hexane		3699		3590	3484	122
3-Methylpentane		3700		3590	3782	124
Cyclohexane		3697		3591	3492	114
	H-ferrierite (Si/Al = 10)					
Initial	3743**	3716	3639	3598		
Propane		3702		3580	3485	113
n-Hexane		3694		3550	3470	128
3-Methylpentane		3708		3550	3470	128
Cyclohexane				Does not change		
	HY (Si/Al = 2.4)					
Initial	3742**			3643	3547	
Propane				3595*	3547	47
n-Hexane				3589*	3545	53
Cyclohexane				3592*	3546	50
	HZSM-5 (Si/Al = 15)					
Initial	3740**	3730	3660	3610		
Propane		3703		3495		115
n-Hexane		3696		3465		145

* Positions of these bands were determined from the difference spectra.
** Positions of these bands does not change after alkane adsorption.

requires additional experimental support, which is beyond the scope of the present work.

The band 3653–3658 cm^{-1} of initial HM zeolite arising from acidic OH groups localized at the extraframework aluminum ions disappears upon alkane adsorption. It is most likely that this band shifts toward lower frequencies and is masked by more intense bands at 3590 and ~3500 cm^{-1}.

A decrease in the intensities of the silanol bands at 3740 cm^{-1}, the disappearance of a shoulder at 3728 cm^{-1} after alkane adsorption, and the appearance of a new band at 3696–3700 cm^{-1} is worth noting. The relative intensity of the latter band is noticeably higher in HM(15), and this correlates with the higher intensity of the band at 3740 cm^{-1} in the initial HM(15) zeolite. This fact points to the possibility of the formation of a weak hydrogen bond of ≡Si(OH) with alkanes mentioned in [10, 11]. After evacuating the sample at room temperature, the band at 3700 cm^{-1} disappears, and the intensity of the band at 3740 cm^{-1} increases (Fig. 2,

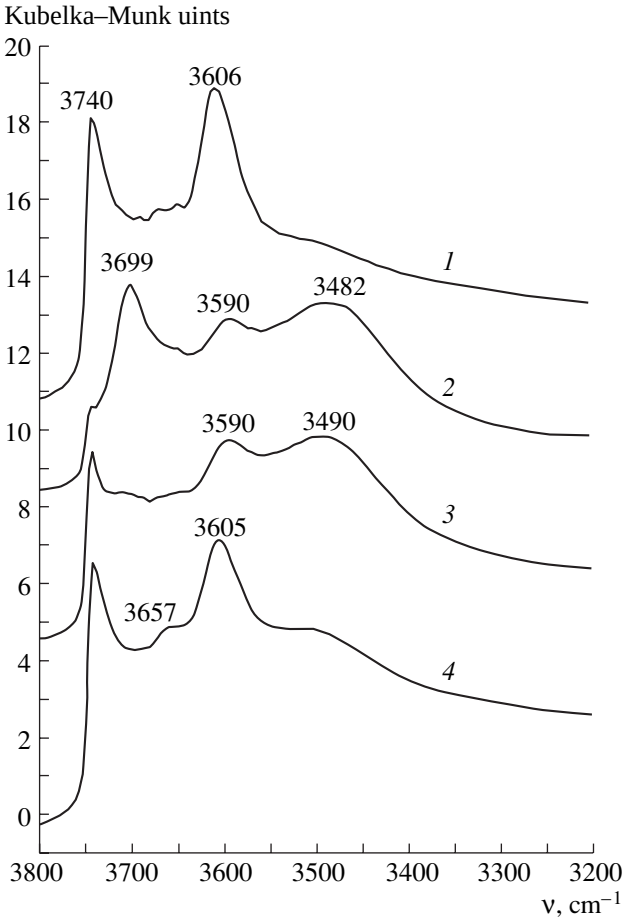

Fig. 2. IR spectra of H-mordenite (Si/Al = 15): (*1*) initial, (*2*) after 3-methylpentane adsorption at 20°C and further evacuation at (*3*) 20 and (*4*) 100°C for 0.5 h.

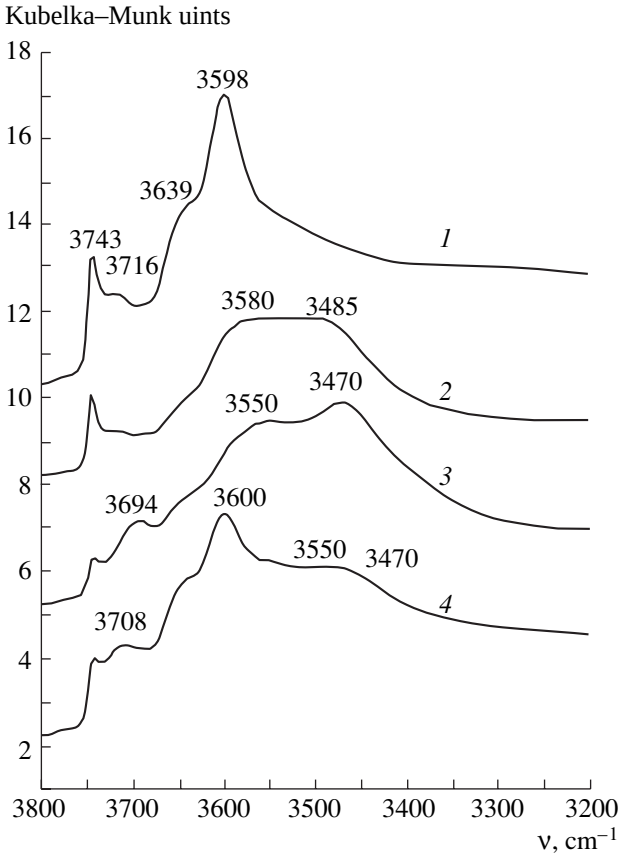

Fig. 3. IR spectra of H-ferrierite (Si/Al = 10): (*1*) initial, (*2*) after propane adsorption, (*3*) after *n*-hexane adsorption, and (*4*) after 3-methylpentane adsorption at room temperature.

spectrum *3*), whereas the stronger complexes of Si(OH)Al groups with alkanes decompose upon evacuation only at a temperature of ~100°C (Fig. 2, spectrum *4*).

Alkane Adsorption on H-Ferrierite

In the IR spectrum of HFer in the region of the stretching vibrations of OH groups, we observed absorption bands at 3743, 3716, 3639, and 3598 cm^{-1} (Fig. 3, Table 1). The most intense band at 3598 cm^{-1} belongs to bridging hydroxy groups of Si(OH)Al and has a complex structure. According to [7], this band consists of at least four overlapping bands at 3609, 3601, 3587, and 3565 cm^{-1}, corresponding to the stretching vibrations of Si(OH)Al groups, which are localized in the 10-membered rings, the large cavities of 8-membered ring channels, and in the 8- and 6-membered rings in the structure of HFer. The accessibility of these bridging hydroxy groups for adsorbate molecules is determined by the geometry of these molecules. The bands at 3743 and 3716 cm^{-1} belong to the silanol groups, and the low-intensity band at 3638 cm^{-1} belongs to OH groups localized at the extraframework aluminum ions.

After exposure of HFer to propane and *n*-hexane at room temperature, the maximum of the adsorption band at 3598 cm^{-1} shifts to 3550–3580 cm^{-1}, and a broad band simultaneously appears with maxima at 3485 cm^{-1} (C_3H_8) and 3470 cm^{-1} (n-C_6H_{14}). Upon the adsorption of 3-methylpentane on HFer, the intensity of the band at 3598 cm^{-1} decreases, but it does not disappear completely. A broad band with maxima at 3550 and 3470 cm^{-1} appears. The adsorption of cyclohexane does not lead to changes in the IR spectrum of OH groups in HFer (Table 1).

These data show that molecules with smaller kinetic diameters (propane and *n*-hexane, $\sigma = 4.3$ Å) may penetrate into both 10-membered ring channels with an opening of 4.2×5.4 Å and 8-membered ring channels with an opening of 3.5×4.8 Å [13]. Only 10-membered ring channels are accessible to 3-methylpentane, whereas cyclohexane molecules ($\sigma = 5.0$ Å) do not penetrate into HFer channels. An attempt was made to estimate the fractions of Si(OH)Al groups accessible to isobutane ($\sigma = 5.0$ Å) and *n*-hexane [7, 8]. These are 23 and 70%, respectively.

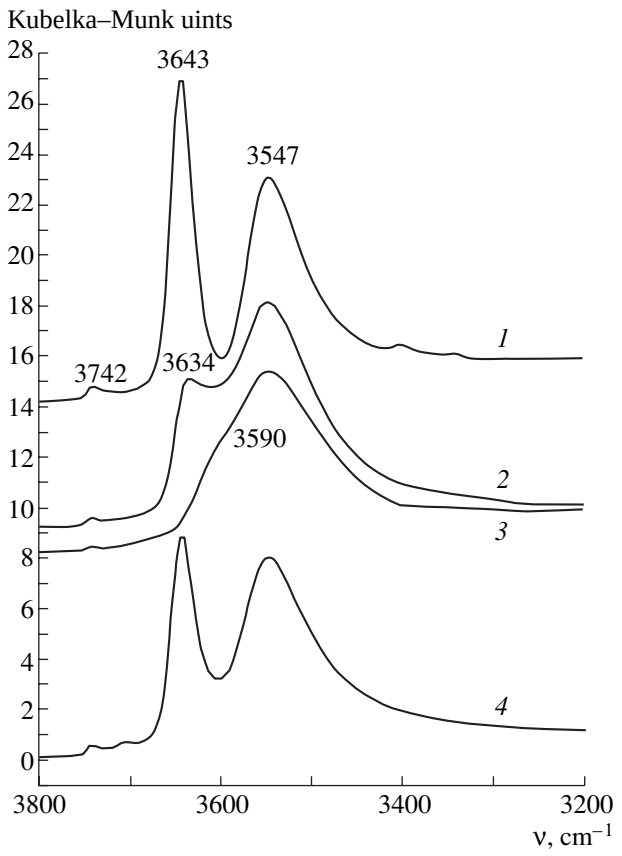

Fig. 4. IR spectra of HY (Si/Al = 2.4): (*1*) initial, (*2*) after propane adsorption, (*3*) after *n*-hexane adsorption, and (*4*) after cyclohexane adsorption at room temperature.

Due to the formation of hydrogen bonds between adsorbed propane and *n*-hexane molecules and bridging Si(OH)Al groups in 10- and 8-membered ring channels of zeolites, the adsorption bands at 3609 and 3601 cm^{-1} shift toward lower frequencies (to 3485 and 3470 cm^{-1}, respectively), whereas Si(OH)Al groups inaccessible to these molecules reveal themselves in the form of individual adsorption bands at 3550–3580 cm^{-1}. In the case of 3-methylpentane adsorption, the adsorption bands at 3600 and 3550 cm^{-1} for Si(OH)Al groups that do not form a hydrogen bond and the bands at 3470 cm^{-1} for Si(OH)Al groups that do form a hydrogen bond with *iso*-C_6H_{14} in 10-membered ring channels are observed.

As in the case of HM, the value of the shift of ΔνOH depends on the nature of the adsorbate and increases in the following series: propane < 3-methylpentane ≈ *n*-hexane (Table 1).

Upon alkane adsorption on HFer, some changes are seen in the region of the absorption bands of silanol groups (Fig. 3, Table 1). A shoulder at 3716 cm^{-1} disappears and the adsorption bands shift by 10–25 cm^{-1} toward lower frequencies appear. These data, as in the case of HM, can be interpreted as the formation of a weak hydrogen bond between ≡Si(OH) and alkanes. The band at 3702–3687 cm^{-1} disappears after the breaf evacuation of the sample at room temperature.

Alkane Adsorption on HY

In the IR spectrum of HY, the following bands are observed in the region of the stretching vibrations of OH groups: absorption bands of terminal silanol groups at 3742 cm^{-1}, a band at 3643 cm^{-1} from bridging Si(OH)Al groups localized in large zeolite cavities, and a band at 3547 cm^{-1} belonging to Si(OH)Al in sodalite cages [9] (Fig. 4, Table 1). Because the sodalite cage opening is small, these hydroxy groups are inaccessible to adsorbed molecules and the band at 3547 cm^{-1} does not shift upon alkane adsorption.

After the contact of propane with the HY zeolite at room temperature, we recorded an IR spectrum shown in Fig. 4 (spectrum *2*). The maximum of the IR band at 3643 cm^{-1} shifts toward lower frequencies to 3634 cm^{-1}. The subtraction of the initial spectrum (spectrum *1*) from spectrum *2* (Fig. 4) makes it possible to determine the true position of the maximum of the shifted band: 3595 cm^{-1} (Table 1). An analogous procedure for spectrum *3* (*n*-hexane adsorption) and *4* (cyclohexane adsorption) gives close values for the maximum of the shifted high-frequency band Si(OH)Al in large cavities (Table 1). The value of ΔνOH for the alkanes studied is within 47–53 cm^{-1}, and it is noticeably lower than ΔνOH for HM and HFer. Note that the value of ΔνOH equal to 85–110 cm^{-1} reported in [9] for the adsorption of normal C_3–C_6 alkanes on HY seems to be highly overestimated. The true position of the maximum of the shifted high-frequency band of Si(OH)Al can only be determined from difference spectra, but this procedure was not used in [9].

As in the case of HM and HFer, the strengths of alkane binding to Si(OH)Al groups in HY depends on the carbon chain length. Adsorbed propane can easily be removed if the sample is evacuated at room temperature, and adsorbed *n*-hexane can be removed from the sample if the temperature of evacuation is as high as 70–120°C.

Alkane Adsorption on HZSM-5

The following bands are observed in the IR spectrum of HZSM-5 in the region of OH-group stretching vibrations: the absorption band of terminal silanol groups at 3740 cm^{-1} with a shoulder at 3730 cm^{-1}, a band at 3660 cm^{-1} of the hydroxyls localized at the extraframework aluminum ions, and an intense band at 3610 cm^{-1} belonging to the stretching vibrations of Si(OH)Al (Fig. 5, spectrum *1*, Table 1). The channel opening in HZSM-5 (5.6 × 5.3 Å [13]) is large enough to allow propane and *n*-hexane molecules (σ = 4.3 Å) to penetrate into channels.

After the exposure of HZSM-5 to propane and *n*-hexane the absorption band of Si(OH)Al disappears

and broad bands at 3495 and 3465 cm^{-1} appear (spectra *2* and *3*, respectively, in Fig. 5). These bands are due to the formation of hydrogen bonds between alkanes and Brønsted acid sites. The band at 3660 cm^{-1} also disappears, probably due to a shift toward lower frequencies and its masking by the intense bands at 3465 and 3495 cm^{-1}.

Changes in the IR spectra in the region of silanol group absorption after propane and *n*-hexane adsorption suggest that these groups are nonuniform. It is likely that the band at 3730 cm^{-1} (Fig. 5, spectrum *1*) corresponds to silanol groups that are capable of forming relatively weak hydrogen bonds with alkanes. As a result, the adsorption bands at 3703 cm^{-1} (propane) and 3696 cm^{-1} (*n*-hexane) appear. The bands completely disappear after evacuating the zeolite sample at room temperature.

DISCUSSION

IR data obtained in this work clearly show that alkanes are adsorbed on hydrogen-exchanged zeolites due to the formation of weak hydrogen bonds with Brønsted acid sites. The formation of a hydrogen bond results in the shift of the absorption bands of Si(OH)Al groups toward lower frequencies, and the value of the shift of ΔνOH depends on the nature of the adsorbed alkane: ΔνOH (propane) < ΔνOH (*n*-hexane) = ΔνOH (3-methylpentane). The strength of the bond between an alkane and an OH group depends on the degree of C–C and C–H bond polarization in alkanes and on the acidic properties of the OH group. Important information on perturbation due to the interaction of alkanes with OH groups can probably be obtained from the IR spectra of alkanes. Unfortunately, detailed analysis of these spectra is only possible for simple molecules such as methane. The IR spectra of C_3 and C_6 alkanes in the region of C–H stretching vibrations, combination of stretching and bending C–H vibrations, and vibration overtones accessible to our measurements proved to be very intricate, and we failed to interpret them unambiguously.

Table 2 compares the positions of the absorption bands of Si(OH)Al in the IR spectra of some hydrogen-exchanged zeolites before and after alkane adsorption. These data were obtained in this work and taken from published data. In the case of HM, our data agree well (within an error of 7 cm^{-1}) with the literature [6, 9]. For HFer, the agreement is somewhat worse: ΔνOH for adsorbed *n*-hexane differs by 11 cm^{-1}, which is probably due to the difference in the Si/Al ratios in the H-ferrierites studied. Because ΔνOH does not change in our experiments when the sample is evacuated and adsorbed hydrocarbons are removed (that is, ΔνOH is independent of the coverage), there is no reason to believe that the difference in ΔνOH for adsorbed *n*-hexane can be due to the difference in the amount of adsorbed alkane. Substantial differences in the ΔνOH value obtained in this work and in [9] are observed for

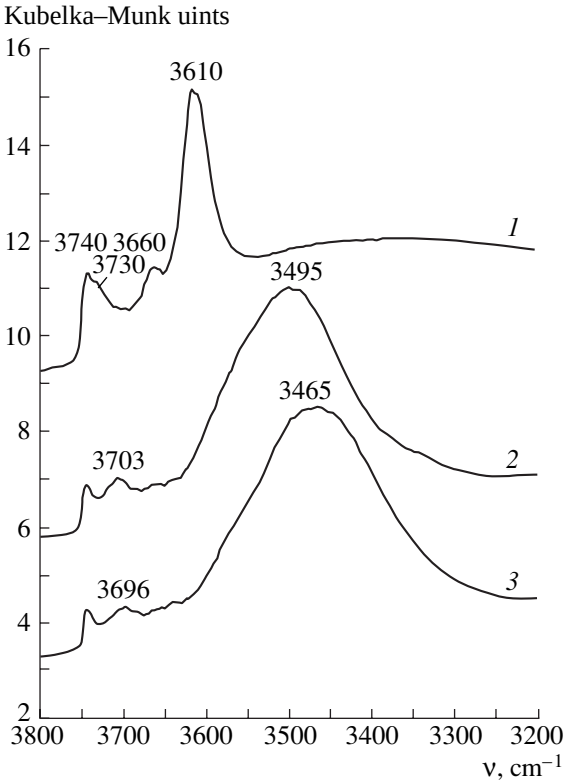

Fig. 5. IR spectra of HY (Si/Al = 15): (*1*) initial, (*2*) after propane adsorption, and (*3*) after *n*-hexane adsorption, at room temperature.

HY. As mentioned above, the value of ΔνOH equal to 86–110 cm^{-1} is overestimated for the case of normal C_3–C_6 alkane adsorption because the procedure of spectra subtraction was not performed in [9]. Finally, a substantial difference in the values of ΔνOH is observed for the adsorption of propane and *n*-hexane on HZSM-5 (Table 2), although the positions of bands for OH groups in the initial zeolite samples agree very well. This fact suggests that some care should be exercised when comparing the spectra of the same zeolites obtained by different authors.

It follows from the data on ΔνOH in the IR spectra of adsorbed alkanes obtained in this work that the strength of Brønsted acid sites decreases in the series HZSM-5 > HM ≈ HFer ≫ HY, and the difference between the three high-silica zeolites are not pronounced. Bordiga *et al*. [4] came to the same conclusion: they measured the values of ΔνOH for HFer when several weak bases (H_2, N_2, and CO) were adsorbed on it and showed that the acidities of Si(OH)Al groups in HFer, HZSM-5, HM, and H-beta are very close. However, more detailed analysis of the IR spectra of the $OH\cdots H_2$ complexes [3] including the comparison of ΔνOH values, the intensities of OH bands, the positions of the H–H stretching bands, and their intensities showed that the acidity decreases in the following series HM > HZSM-5 > HM. Thus, IR data for different

Table 2. Absorption bands of Si(OH)Al groups in the IR spectra of hydrogen-exchanged zeolites and their shifts upon alkane adsorption

Zeolite	ν(Si–OH–Al), cm^{-1}	Δν(Si–OH–Al), cm^{-1}						Ref.
		propane	*n*-butane	*n*-pentane	*n*-hexane	3-methyl-pentane	cyclohexane	
H-mordenite								
Si/Al = 7.7	3607						107	[6]
Si/Al = 10	3607	97	→	→	115			[9]
Si/Al = 5	3606	101			119		109	This work
Si/Al = 15	3606				122	124	114	This work
H-ferrierite								
Si/Al = 6.3	3602				117			[7, 8]
Si/Al = 10	3598	113			128	128		This work
HY								
Si/Al = 2.7	3645, 3545	85	→	→	110			[9]
Si/Al = 2.4	3642, 3547	47			53		50	This work
HZSM-5								
Si/Al = 35	3610	92	→	→	110			[9]
Si/Al = 23	3612		127		152*			[10, 11]
	3610				136			[7]
Si/Al = 15	3610	115			145			This work

Note: Arrows mean that Δν increases with an increase in the carbon chain length [9].
∗ Δν for *n*-heptane.

probe molecules lead us to the conclusion, which is qualitatively the same and well known, that the acidity of high-silica zeolites is considerably higher than the acidity of faujasites. However, finer differences in the acidity inside the group of high-silica zeolites are not clearly seen from the results of different authors.

To conclude, we would like to draw attention to the formation of weak hydrogen bonds between terminal silanol groups and alkanes. Most researchers (except Trombetta *et al*. [10, 11]) did not analyze the spectra in the region of ~3740 cm^{-1} and ignored the formation of SiOH…RH complexes. At the same time, weakly acidic silanol groups in HM, HFer, and HZSM-5 may contribute to the overall acidity of these zeolites and should be taken into account when considering the mechanisms of acid–base catalyzed reactions.

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