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The study of heterogeneity of OH groups in zeolites by comparing the half-width of IR band of hydroxyls interacting with adsorbed molecules

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Abstract

We propose a method of the studies of heterogeneity of OH groups in zeolites by comparing the half-width of the band of OH groups interacting with adsorbed molecules with that of homogenous acidic hydroxyls. We determined a correlation between half-width ($\Delta\nu_{1/2}$) and frequency shift ($\Delta\nu$) for homogenous OH groups in phenol, acetic acid, trifluoroacetic acid, and on SiO_2 surface as well as in NaHX zeolite ($Si/Al = 1.0$) interacting with various electrodonor molecules (*n*-hexane, benzene, toluene, *p*-xylene, ethene, propene, butene-1, acetonitrile and diethyl ether). The application of our correlation to the problem of heterogeneity of OH groups in zeolites was tested for homogenous OH groups in NaHA and dealuminated H-beta zeolite and heterogeneous OH groups in H-mordenite and H-beta. We used the $\Delta\nu_{1/2}$–$\Delta\nu$ correlation to study the problem of heterogeneity of OH groups in H-ZSM-5 zeolites in which some previous studies suggested heterogeneity and some others homogeneity of OH groups. We also studied the problem of heterogeneity of P–OH groups in cloverite. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Heterogeneity; Zeolites; Half-width

1. Introduction

Acid properties of zeolites determine the catalytic activity in many important reactions — they are intensively studied in numerous laboratories. IR spectroscopy is one of the most important methods for the investigation of acidity of zeolites. Many important papers concerning IR studies of zeolite acidity and basicity were published by Lavalley and his collaborators (e.g. Refs. [1–7]). The study of acidity of zeolites consists of the determination of concentration of Bronsted and Lewis acid sites, characterization of their acid strength and studying the problem of heterogeneity of OH groups. Heterogeneity of OH groups in zeolites has been studied in our laboratory in last years [8–12]. Two methods have been used to decide if OH groups in zeolites were homo- or heterogeneous. One of them was following the position of IR band of free OH restoring during the stepwise desorption of bases such as ammonia or pyridine at increasing temperatures [9,13,14]. In the case of heterogeneous OH groups, less acidic hydroxyls of higher stretching frequency release adsorbed bases at lower temperatures than more acidic hydroxyls (of lower frequency), and, therefore, the band of free OH shifts to lower frequencies with desorption temperature.

Another method was the analysis of IR band of OH groups interacting with aromatic hydrocarbons by hydrogen bonding and with alkanes by “permanent dipole–induced dipole interaction” [9–11]. In the case of heterogeneous OH groups, the shifted band

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is large and split into several submaxima. Practically, in all the cases, the splitting is seen only after calculation of the second derivatives of spectra (after careful smoothing). Analysis of the second derivative may however bring some artefacts because noises and other "imperfections" of spectra may produce strong effects in the second derivative diagrams. To minimalize such artefacts, we always compared a series of spectra recorded upon the adsorption of various amounts of hydrocarbons, i.e. spectra in which various amounts of OH groups are engaged in hydrogen bonding. Only the effects appearing in the whole series of spectra were taken into consideration.

Now we propose a third method of IR studies of heterogeneity of OH groups in zeolites: by comparing the half-width ($\Delta\nu_{1/2}$) of the band of hydrogen-bonded OH groups in the studied zeolite with the half-width of hydrogen-bonded homogenous OH groups. We made, therefore, the correlation diagram of the values of half-width and frequency shift ($\Delta\nu$) for hydrogen-bonded acidic homogenous hydroxyls. If the half-width of IR band of OH hydrogen-bonded groups in the zeolite studied is distinctly higher than that obtained for homogenous OH groups for the same $\Delta\nu$ (taken from the correlation diagram) one can suppose that our zeolitic hydroxyls are heterogeneous and the IR band of hydrogen-bonded OH groups composes of several submaxima. To find the correlation diagram, following systems containing acidic homogenous OH groups were studied: phenol, acetic acid, trifluoroacetic acid, SiO_2 (surface Si–OH groups were studied) and NaHX zeolite. Our earlier IR study [9] evidenced that NaHX zeolite contained only homogenous $(AlO)_3Si–OH–Al(SiO)_3$ groups. Benzene, toluene, *p*-xylene, acetonitrile, diethyl ether, ethene, propene, and 1-butene were used as electron donors when studying hydrogen bonding and *n*-hexane was used when studying "permanent dipole–induced dipole interaction".

Our correlation between the values of half-width ($\Delta\nu_{1/2}$) and frequency shifts ($\Delta\nu$) for homogenous OH groups was compared with similar correlations obtained by other authors for dissolved phenol and methanol [15,16]. Such correlations were not studied before for OH groups on solid surfaces.

The proposed method of the studies of heterogeneity of OH groups based on the correlation: half-width ($\Delta\nu_{1/2}$) and frequency shifts ($\Delta\nu$) was tested for OH groups in NaHA, NaHY, H-mordenite, H-beta and dealuminated H-beta. It was also applied when studying the heterogeneity of OH groups in H-ZSM-5 in which the situation is not clear: there are some arguments for homogeneity [17,18] and some others [8,12,19] for heterogeneity of OH. We also applied it to the problem of OH groups in cloverite.

2. Experimental

Acetic acid, trifluoroacetic acid, *n*-hexane, phenol, benzene, toluene, *p*-xylene, acetonitrile, diethyl ether (POCh Gliwice, chem. pure) ethene, propene, and 1-butene (Union Carbide >99% pure) were used.

We also used SiO_2 (Aerosil-Degussa) and zeolites: $NaNH_4X$ ($Si/Al = 1.0$, Na/NH_4 exch. deg 30%), $NaNH_4A$ ($Si/Al = 1.0$, Na/NH_4 exch. deg 25%), H-ZSM-5($Si/Al = 15$), H-mordenite ($Si/Al = 5.8$), H-beta ($Si/Al = 10$, Ref. [13]) and dealuminated H-beta ($Si/Al = 70$, Ref. [13]).

The spectra of gaseous phenol, acetic acid, and trifluoroacetic acid were recorded at room temperature in 10 cm IR gas cell.

IR spectra of phenol, acetic acid, trifluoroacetic acid dissolved in *n*-hexane, benzene, toluene, *p*-xylene, acetonitrile, diethyl ether (ca. $0.05\,mol/dm^3$) were recorded in 0.1 mm NaCl cell. SiO_2, $NaNH_4X$ and H-ZSM-5 zeolites were activated at vacuum 1000, 620 and 770 K, respectively, other zeolites at 720 K for 1 h. *n*-Hexane, benzene, toluene, *p*-xylene, acetonitrile, diethyl ether, ethene, propene, and butene-1 were adsorbed at room temperature. The amount of adsorbed probe molecules was always 60–90% of the amount of OH groups. All the spectra were recorded on BRUKER IFS 48 spectrometer.

3. Results and discussion

3.1. Correlation of half-width and frequency shift for homogenous OH groups

The stretching frequencies of free OH groups in gaseous phenol, acetic acid and trifluoroacetic acid are 3657, 3579 and $3583\,cm^{-1}$, respectively.

The spectra of OH groups in these three acids interacting with *n*-hexane, benzene, toluene, *p*-xylene,

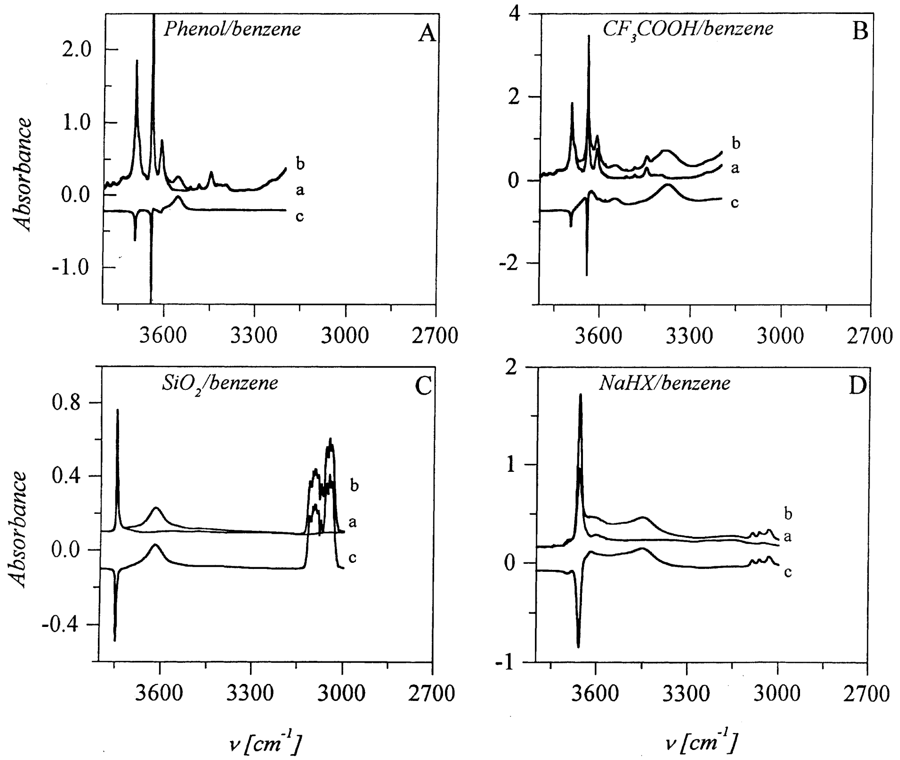

Fig. 1. IR spectra of OH groups in phenol (A) and trifluoroacetic acid (B) dissolved in benzene: (a) benzene, (b) solution (ca. 0.05 mol/dm^3 in 0.1 mm cell), (c) difference spectra (b − a). IR spectra of OH groups on SiO_2 (C) and in NaHX (D) interacting with benzene (a) activated SiO_2 (or NaHX), (b) after benzene adsorption, (c) difference spectra (b − a).

acetonitrile and diethyl ether were recorded in solutions. The spectra of all the solvents and solutions were recorded and subsequently difference spectra were calculated. The spectra obtained for phenol and trifluoroacetic acid interacting with benzene are presented in Fig. 1A and B as examples. The bands of OH in trifluoroacetic acid perturbed by the interaction with the electron donors (normalized to the same intensity) are presented in Fig. 2A. The values of frequency shifts ($\Delta\nu$) as well as of band half-widths ($\Delta\nu_{1/2}$) for both the acids and all the electron donors are summarized in Table 1.

To study the IR bands of surface OH groups on SiO_2 and in NaHX zeolite interacting with electron donors, *n*-hexane, benzene, toluene, *p*-xylene, acetonitrile, diethyl ether, ethene, propene, and 1-butene were adsorbed. The results obtained with the adsorption of benzene are presented in Fig. 1C and D as examples. The bands of perturbed OH on SiO_2 surface (normalized to the same intensity) are presented in Fig. 2B as examples. The values of frequency shifts ($\Delta\nu$) as well as of band half-widths ($\Delta\nu_{1/2}$) are summarized in Table 1.

All the data either obtained with organic acids or surface OH groups fit the same correlation presented in Fig. 3A. The dependence of half-width and frequency shift of IR band of hydrogen-bonded OH groups was studied by several authors [15,16], it was also the subject of quantum-chemical calculations of Sakun and Sokolov [20]. The results of Huggins and Pimentel [15], and of Glew and Rath [16] are presented in Fig. 3B and compared with our correlation line. The data of Glew and Rath [16], obtained with methanol at room temperature, agree well with our line. On the other hand, higher $\Delta\nu_{1/2}$ values were reported by Huggins and Pimentel [15]. These authors

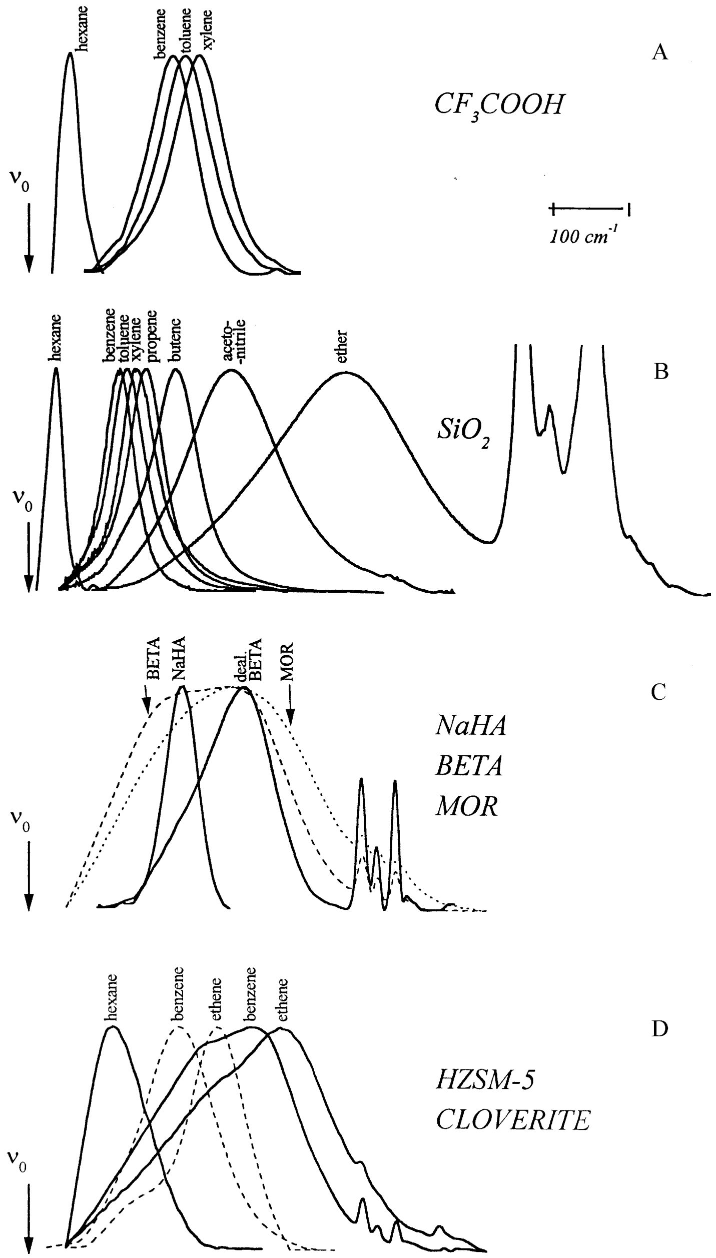

Fig. 2. (A), (B) OH groups in trifluoroacetic acid and on SiO_2 surface interacting with electrodonor molecules; (C) OH groups in NaHA (interacting with ethene), and H-mordenite, H-beta, dealuminated H-beta (interacting with benzene); (D) OH groups in H-ZSM-5 (solid lines) and cloverite (dashed lines) interacting with *n*-hexane, benzene and ethene. In order to compare better the band shifts and half-widths, the bands of free OH were located at the same positions and the bands of perturbed OH were normalized to the same intensity. In Figs. C and D, the C–H bands of ethene and benzene were reduced by the subtraction of spectra of liquid benzene and gaseous ethene.

Table 1
The frequency shifts ($\Delta\nu$) and half-width ($\Delta\nu_{1/2}$) values of IR bands of OH groups in phenol, acetic acid, trifluoroacetic acid, SiO_2 and NaHX zeolite interacting with electrodonor molecules

Adsorbate	Phenol, $\nu_0 = 3657\,cm^{-1}$		CH_3COOH, $\nu_0 = 3579\,cm^{-1}$		CF_3COOH, $\nu_0 = 3583\,cm^{-1}$		SiO_2, $\nu_0 = 3748\,cm^{-1}$		NaHX, $\nu_0 = 3668\,cm^{-1}$	
	$\Delta\nu$	$\Delta\nu_{1/2}$	$\Delta\nu$	$\Delta\nu_{1/2}$	$\Delta\nu$	$\Delta\nu_{1/2}$	$\Delta\nu$	$\Delta\nu_{1/2}$	$\Delta\nu$	$\Delta\nu_{1/2}$
Hexane	35	12	34	12	60	32	43	35	–	–
Ethene	–	–	–	–	–	–	140	54	265	124
Benzene	101	30	112	42	206	77	139	64	210	88
Toluene	108	22	123	40	226	80	151	62	224	101
p-Xylene	113	32	133	43	238	84	162	63	272	136
Propene	–	–	–	–	–	–	183	65	344	178
Butene-1	–	–	–	–	–	–	229	86	430	204
Acetonitrile	–	–	303	153	–	–	318	171	–	–
Diethyl ether	323	124	–	–	–	–	485	283	–	–

used however, the values of stretching frequencies of methanol and phenol dissolved in CCl_4 as values of unperturbed OH groups. As the interaction with CCl_4 decreases the OH frequency, we recalculated the $\Delta\nu$ values of Huggins and Pimentel [15] using the values concerning really unperturbed hydroxyls, i.e. these in gaseous methanol and phenol (3687 and 3657 cm^{-1}, obtained in this study). These recalculated values agree well with our results and also with those of Glew and Rath [16].

The correlation between $\Delta\nu_{1/2}$ and $\Delta\nu$ found in our study (Fig. 3A) has a general character. It is obeyed both by acidic hydroxyls in organic molecules (phenol, acetic acid and trifluoroacetic acid) and also by acidic hydroxyls on solid surfaces (SiO_2 and in NaHX). It is also obeyed by hydroxyls of various acidity: the points characterizing less acidic hydroxyls and strong electron donors as well as more acidic hydroxyls and weak electron donors fit the same line.

The fact that our correlation between $\Delta\nu_{1/2}$ and $\Delta\nu$ is so general and will be helpful in its application to the studies of heterogeneity of OH groups in zeolites. The points characterizing homogenous hydroxyls independently of their acidity fit the same line. The fact that half-width of the band of hydrogen-bonded zeolitic OH groups is distinctly higher than the value for homogenous OH obtained from our correlation for the same $\Delta\nu$ suggests, that these hydroxyls are heterogeneous and the IR band consists of several submaxima. Of course, such a thesis has to be verified by calculation of the second derivative and by the study of the position of IR band of free OH restoring at ammonia desorption.

It should be noted that our correlation was obtained on the basis of spectra recorded at room temperature. The experimental data [21,22], as well as quantum-chemical calculations [23,24], evidenced that the half-width of IR band of OH groups engaged in hydrogen bonding depended on temperature (the band narrowed with temperature decrease). Therefore, the half-width of the band of OH groups interacting with molecules such as N_2, CO or Ar at liquid nitrogen temperature cannot be compared with our correlation line. Only the results obtained at room temperature can be taken into account.

3.2. OH groups in zeolites

3.2.1. NaHA zeolite

Our earlier study [25] evidenced that Si–OH–Al groups in NaHA zeolite, similarly as in NaHX were homogenous. It was explained by the presence of only Si(4Al) [26], and, therefore, only $(AlO)_3$Si–OH–Al$(SiO)_3$ groups and also by the fact that in NaHA zeolite of low exchange degree (such as used in our study) only Si–O_1H–Al of the same bridge geometry were present.

Homogenous OH in NaHA zeolite were used to test the possible application of our $\Delta\nu_{1/2}$–$\Delta\nu$ correlation for the study of heterogeneity of OH groups in zeolites. The spectra of OH groups in NaHA interacting with ethene are presented in Fig. 4A, and the band of perturbed OH is shown in Fig. 2C. The $\Delta\nu$ was

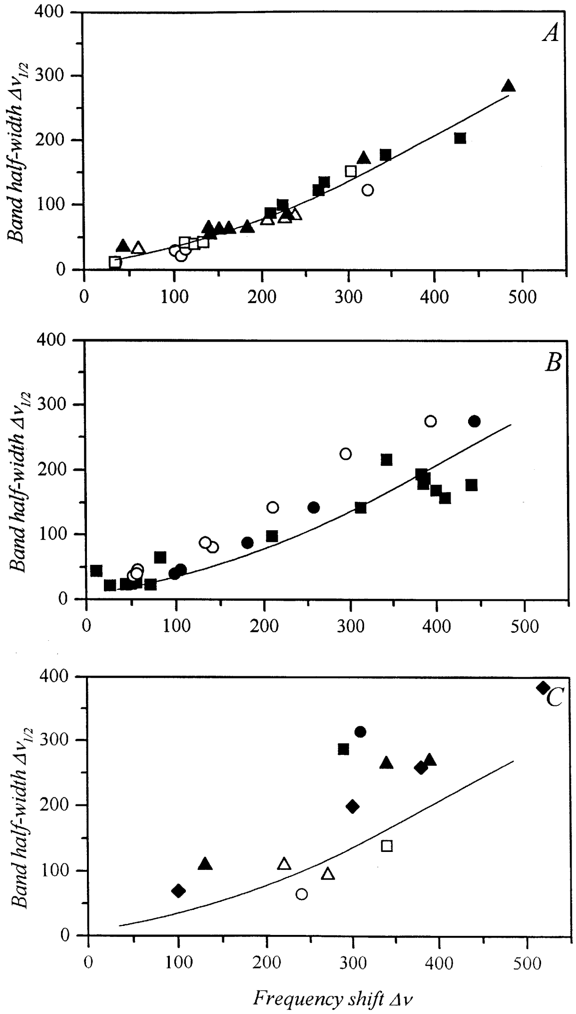

Fig. 3. (A) The correlation between $\Delta\nu_{1/2}$ and $\Delta\nu$ for homogenous OH groups in phenol (○), acetic acid (□), trifluoroacetic acid (△), SiO_2 (▲), and NaHX zeolite of Si/Al = 1.0 (■). (B) The $\Delta\nu_{1/2}$ $\Delta\nu$ correlation determined in A (only the line is presented): (■) data from Ref. [16], (○) data from Ref. [15], (●) data from Ref. [15] corrected with the values of gaseous phenol and methanol. (C) The $\Delta\nu_{1/2}$ $\Delta\nu$ correlation determined in A for homogenous OH groups (only the line is presented), and the values obtained for NaHA (○), H-mordenite (●), H-beta (■), dealumianted H-beta (□), H-ZSM-5 (▲), H-ZSM-5 from Ref. [30] (◆), and cloverite — data from Refs. [31,33] (△).

240 cm^{-1} and $\Delta\nu_{1/2}$ was 65 cm^{-1}. The $\Delta\nu_{1/2}$ value is a little below the $\Delta\nu_{1/2}$–$\Delta\nu$ correlation line (Fig. 3C), in agreement with the fact that these OH groups are homogenous.

3.2.2. H-mordenites and H-beta zeolites

OH groups in H-mordenites are localized in 10-ring and 8-ring channels. Only hydroxyls in 10-ring channels are accessible to reactant molecules and are the active sites in catalytic reactions. We studied [14,27] heterogeneity of these OH groups by the adsorption of CO (at 170 K) and benzene (at room temperature), and also by following the frequency of the band of free OH restoring at pyridine desorption. The obtained results [14,27] suggested heterogeneity of OH groups in H-mordenite of Si/Al = 6.6 due to the presence of $(AlO)(SiO)_2Si–OH–Al(SiO)_3$ and $(SiO)_3Si–OH–Al(SiO)_3$.

Heterogeneous OH groups were found in H-beta of Si/Al = 10; on the other hand, practically homogenous OH were present in dealuminated H-beta (Si/Al = 70) in which practically only $(SiO)_3Si–OH–Al(SiO)_3$ existed [13]. Heterogeneous OH groups in H-mordenite and H-beta and homogenous in dealuminated H-beta were also used to test the application of our $\Delta\nu_{1/2}$–$\Delta\nu$ correlation as a method of the studies of heterogeneity of OH groups in zeolites.

The spectra were recorded upon the adsorption of benzene in H-mordenite and in H-beta and the spectra obtained with non-dealuminated zeolites are presented in Fig. 4B and C as examples. The spectra of OH groups in H-mordenite and H-beta hydrogen-bonded to benzene are presented in Fig. 2C and the values of $\Delta\nu$ and $\Delta\nu_{1/2}$ are given in Table 2 and in Fig. 3C. For dealuminated beta zeolite, in which earlier studies have shown [13] that OH groups were homogenous, the points fit the correlation line, whereas for heterogeneous OH in non-dealuminated zeolites the points are above the line.

The results obtained for mordenite and beta zeolites together with those obtained for NaHA are evidence that our correlation $\Delta\nu_{1/2}$–$\Delta\nu$ may be helpful in the studies of heterogeneity of OH groups in zeolites. Now it will be applied to the problem of heterogeneity of OH groups in H-ZSM-5 and cloverite.

3.2.3. H-ZSM-5 zeolite

Our correlation $\Delta\nu_{1/2}$–$\Delta\nu$ was used to study the problem of heterogeneity of OH groups in H-ZSM-5. Our earlier IR study [8,12] suggested heterogeneity of OH groups in H-ZSM-5. On the other hand, the constant value of adsorption heat of ammonia and pyridine

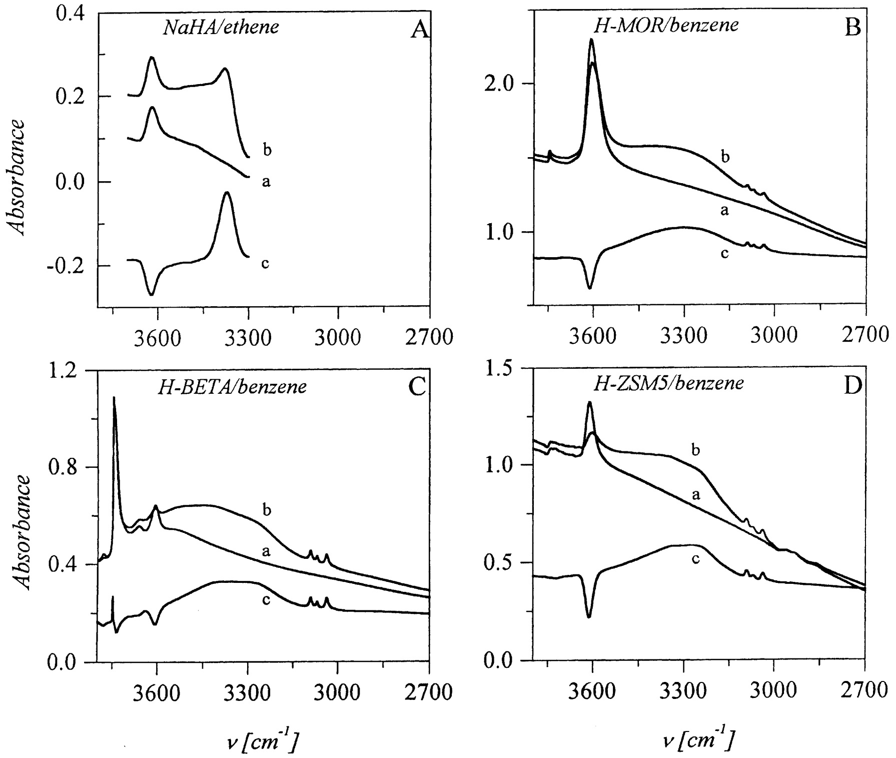

Fig. 4. OH groups in zeolites NaHA (A), H-mordenite (B), H-beta (C) and H-ZSM-5 (D), interacting with ethene and benzene: (a) activated zeolites; (b) after ethene and benzene sorption; (c) difference spectra.

Table 2
The frequency shifts ($\Delta\nu$) and half-width ($\Delta\nu_{1/2}$) values of IR bands of OH groups in zeolites: NaHA, H-mordenite, H-beta, dealuminated H-beta, H-ZSM-5 and cloverite (data from Ref. [31,33]) interacting with *n*-hexane, benzene and ethene

Adsorbate	NaHA $\nu_0 = 3620\,\mathrm{cm}^{-1}$		H-mordenite $\nu_0 = 3611\,\mathrm{cm}^{-1}$		H-beta $\nu_0 = 3608\,\mathrm{cm}^{-1}$		Dealuminated H-beta $\nu_0 = 3608\,\mathrm{cm}^{-1}$		H-ZSM-5 $\nu_0 = 3610\,\mathrm{cm}^{-1}$		Cloverite $\nu_0 = 3676\,\mathrm{cm}^{-1}$	
	$\Delta\nu$	$\Delta\nu_{1/2}$	$\Delta\nu$	$\Delta\nu_{1/2}$	$\Delta\nu$	$\Delta\nu_{1/2}$	$\Delta\nu$	$\Delta\nu_{1/2}$	$\Delta\nu$	$\Delta\nu_{1/2}$	$\Delta\nu$	$\Delta\nu_{1/2}$
n-Hexane	–	–	–	–	–	–	–	–	130	110	–	–
Benzene	–	–	310	315	290	288	340	140	340	265	220	110
Ethene	240	65	–	–	–	–	–	–	390	270	270	95

[17,18] suggested homogeneity of OH groups. The results of catalytic studies also give ambiguous results: there are some arguments for heterogeneity [28] and some others for homogeneity [29] of OH groups.

In the present study, we compared the values of half-width of IR bands of OH groups in H-ZSM-5 interacting with *n*-hexane, benzene and ethene with those for homogenous OH groups, obtained from our $\Delta\nu_{1/2}$–$\Delta\nu$ correlation. The spectra recorded upon the adsorption of benzene are presented in Fig. 4D. The bands of perturbed hydroxyls are presented in Fig. 2D. The values of $\Delta\nu$ and $\Delta\nu_{1/2}$ are summarized in Table 2, and are presented in Fig. 3C. The points are above the correlation line for homogenous OH groups, thus suggesting heterogeneity of OH groups in H-ZSM-5. Similar conclusion can also be drawn from the results of Zecchina et al. [30] who reported the $\Delta\nu$ and $\Delta\nu_{1/2}$ values for hydrogen-bonded OH groups in H-ZSM-5. These data are also presented in Fig. 3C, the points are above our correlation line thus suggesting the heterogeneity of OH groups.

We suppose that heterogeneity of OH groups in highly siliceous ZSM-5 zeolite may be due to the presence of $(SiO)_3Si–OH–Al(SiO)_3$ of various bridge geometry. It should be noted that the recent results of synchrotron and neutron diffraction studies [19] suggested that at least three kinds of OH groups in various positions could be present in H-ZSM-5.

3.2.4. *Cloverites*

IR spectra of cloverites show two distinct bands of P–OH (3670 cm^{-1}) and Ga–OH (3700 cm^{-1}). The P–OH groups were found to be weakly acidic, they reacted with pyridine forming pyridinium ions [31]. This reaction was reversible and desorption restored P–OH groups. P–OH groups formed hydrogen bonding with CO, benzene and ethene thus resulting in a red shift of 3670 cm^{-1} band. There were no literature data on heterogeneity of P–OH groups in cloverite. We studied this problem using our $\Delta\nu_{1/2}$–$\Delta\nu$ correlation. The values of $\Delta\nu$ and $\Delta\nu_{1/2}$ were taken from the papers of other authors [31–33]. These values are presented in Table 2 and in Fig. 3C. The points fit the correlation line, thus suggesting that P–OH groups in cloverite are homogenous.

We suppose that homogeneity of P–OH groups in cloverite may be due to the fact that contrary to bridging hydroxyls in zeolites, all the hydroxyls in cloverite are terminal. They have the same geometry and are attached to one type of rings (D4Rs) protruding into the window.

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