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Heterogeneity of OH Groups in NaH-ZSM-5 Zeolite Studied by Infrared Spectroscopy

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The properties of the OH groups in NaH-ZSM-5 zeolite absorbing at 3609 cm^{-1} were studied with respect to their hydrogen bonding to weak electron donor molecules (*n*-hexane, fluorobenzene, chlorobenzene, benzene, toluene, *p*-xylene, ethene). The observed band splitting was attributed to the heterogeneity of the OH groups. A comparative study of systems with homogeneous OH groups did not show such a splitting. The Bellamy–Hallam–Williams (BHW) relation was obeyed for all kinds of OH groups, and the proton affinities (PA) were calculated from this relation. Two probable explanations of the heterogeneity of OH groups in NaH-ZSM-5 zeolite are considered. One assumes the presence of OH groups with various numbers of Al atoms in the immediate neighborhood, and the other (more plausible) assumes dependence of OH acid strength on Si–O and Al–O bond lengths and Al–OH–Si bond angles.

INTRODUCTION

Zeolite OH groups which are active sites in various acid-catalyzed reactions have been subject to extensive studies. The main results have been summarized in several monographs [e.g., Refs. (*1–3*)]. This paper deals with heterogeneity of the OH groups in NaH-ZSM-5 zeolite which absorb in the infrared at 3609 cm^{-1}. Two general theoretical approaches were proposed. One, presented by Mortier *et al.* (*4–6*), is based on the collective model of zeolite acidity and assumes the existence of only one kind of OH group, the acid properties of which are dependent only on the overall composition of zeolite. The collective model explains well the linear dependence of various parameters characterizing the acid and catalytic properties of zeolites on average electronegativity. Another point of view was presented by Kazanski (*7*). According to this author the properties of OH groups are influenced only by the number of Si and Al atoms situated in their immediate neighborhood. Such a "local approach" calls for the existence of several kinds of OH groups in zeolites.

Several experimental results suggest that there is heterogeneity of OH groups in zeolites. The heat of NH_3 adsorption in NaH-ZSM-5 (*8, 9*) and in mordenite (*10*) decreases with the amount of ammonia reacting with strong sites. Even though the vibration frequency of free OH groups depends only very slightly on their acid strength (*11, 12*), Dombrowski and Hoffmann (*13*) and also Dźwigaj *et al.* (*14*) observed the splitting of the OH bands in hydrogen and cationic forms of Y zeolites. The IR band of OH groups in NaH-ZSM-5 zeolite forming a hydrogen bond with benzene molecules was asymmetric and split (*15, 16*).

None of these results, however, is definite proof of the heterogeneity of OH groups in zeolites. The microcalorimetric results concern not only Brønsted but also Lewis acid sites. The splitting of the band of OH groups participating in hydrogen bonding with benzene may be due not only to the heterogeneity but also to other reasons which will be considered in the present paper. The goal of our research was to establish whether the observed splitting is indeed due to heterogeneity of OH groups and to study their acidity in a more quantitative way.

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EXPERIMENTAL

Materials. The NH_4 form of ZSM-5 zeolite $Na_{0.3}(NH_4,H)_{1.7}(AlO_2)_2(SiO_2)_{94}$ was obtained by ionic exchange of the parent sodium form (''Ultrazet'') synthesized at the Institute of Industrial Chemistry (Warsaw).

SiO_2 (Aerosil) was obtained from Degussa. All adsorbates—*n*-hexane (Fluka), fluorobenzene (Loba Chemie), chlorobenzene (Koch–Light), benzene, toluene, and *p*-xylene (POCH Gliwice)—and all standard acids—acetic, benzoic, chloroacetic, trichloroacetic, trifluoroacetic, ethanol, and phenol (POCH Gliwice)—were used as purchased.

Adsorption on SiO_2 and NaH-ZSM-5 zeolite. Spectra were recorded using a Specord 75 IR spectrometer working ''on line'' with a KSR 4100 minicomputer. For the IR studies the zeolite and SiO_2 were pressed into thin wafers (zeolite, 6–8 mg cm^{-2}; SiO_2, 3–4 mg cm^{-2}). The wafers were activated *in vacuo* at 770 K (zeolite) and 1070 K (SiO_2) for 1 h. Portions of adsorbates (*n*-hexane, fluorobenzene, chlorobenzene, benzene, toluene, and *p*-xylene) were introduced at room temperature into the cell. To avoid oligomerization, the adsorption of ethene was studied at 200 K. The difference between the spectra recorded before and after the adsorption was the spectrum of the OH groups interacting with adsorbed species.

Organic acids, phenol, and ethanol in gaseous phase and in solutions. The spectra of gaseous acetic and trifluoroacetic acids and also of ethanol were recorded at room temperature in a 10-cm gas cell. The spectra of gaseous benzoic, chloroacetic, and trichloroacetic acids and phenol were recorded at higher temperature (about 320 K). Frequencies of free OH groups (ν_{mon}) are presented in Table 1. For spectral studies of the interaction of OH groups with electron donor molecules, diluted solutions (5×10^{-2} mol $liter^{-1}$) of all the acids and phenol in *n*-hexane, fluorobenzene, chlorobenzene, benzene, toluene, and *p*-xylene were used. The spectra of pure solvents were always subtracted from the spectra of solutions. Frequency shifts ($\Delta\nu$) for the interaction of OH groups with electron donor molecules are presented in Table 1.

RESULTS AND DISCUSSION

The data presented in Table 1 show that the frequencies of free acidic OH groups in carboxylic acids are practically independent of their acid strength. This observation is consistent with an earlier report (*12*) and

TABLE 1

Frequencies of Free OH Groups (cm^{-1}) and $\Delta\nu$ (cm^{-1}) in Various Solvents or with Various Adsorbates

	Standard acid								Zeolitic OH group				
	Ethanol	Phenol	Acetic acid	Benzoic acid	Chloro-acetic acid	Tri-chloro-acetic acid	Tri-fluoro-acetic acid	SiO_2	OH(1)	OH(2)	OH(3)	OH(4)	OH(5)
OH group:	3668	3657	3581	3585	3585	3582	3583	3741	3609				
After dissolving in									After the adsorption				
n-Hexane	25	32	39	31	45	56	60	43		86	123	170	202
Fluorobenzene		52	60	57	90	116	120	74	119	188	249	289	328
Chlorobenzene	60	82	88	96	121	166	175	97	188	245	310	365	400
Benzene	65	100	121	139	139	197	205	127	170	285	361	415	
Toluene	67	102	123	129	161	210	222	136	249	336	415	476	
p-Xylene	72	113	133	144	168	227	240	155	274	354	451		
Ethene								143		310	400	440	

indicates that the frequency of free OH groups cannot be used as the measure of their acid strength. Thus, the presence of only one OH band in the spectrum of the zeolite does not preclude existence of OH groups of different acid strength.

Hydrogen bonding of OH groups with electron donor molecules results in a shift of the OH band to lower frequency and in a distinct increase in its intensity (due to an increase in O–H bond polarity) (*12*). With the relatively weak bases used in our study the frequency shift ($\Delta\nu$) can be used as a measure of the acid strength of OH groups. With stronger bases, however, this method fails.

As already mentioned, the 3609 cm^{-1} band of OH groups in NaH-ZSM-5 zeolite forming the bond is asymmetric and split. Several reasons for such an appearance of the spectrum can be considered:

(i) The zeolitic OH groups are heterogeneous; i.e., there are several kinds of OH group of various acid strength resulting in different frequency shifts ($\Delta\nu$) on the hydrogen bonding.

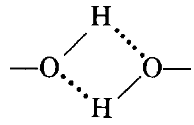
(ii) The local electrical field in zeolites affects the adsorbate molecules differently. The molecules could also assume different geometrical positions in zeolitic channels, resulting in different strengths of hydrogen bonding.

(iii) The shifted OH band is asymmetric because of the overlap of overtone and combination bands of lower-frequency fundamentals enhanced by Fermi resonance. This is observed, for instance, in dimers of carboxylic acids.

It was therefore a matter of considerable importance to distinguish between these possible reasons for band splitting. Case (iii) can be easily verified using systems in which OH groups are homogeneous. Two such model systems were chosen: (a) carboxylic acids and phenol, and (b) surface OH groups on SiO_2 activated at high temperature.

OH Groups in Carboxylic Acids and Phenol

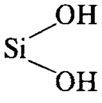
Figure 1A is the spectrum of gaseous trifluoroacetic acid. The OH band of the monomer (3538 cm^{-1}) and a broad and split band of OH groups in dimers



are present. Figure 1B is the spectrum of OH groups in trifluoroacetic acid dissolved in toluene. The band of OH groups forming the hydrogen bond with toluene is symmetric and not split. This is a typical example of an organic acid dissolved in a weakly basic organic solvent; analogous spectra were obtained with other acids (acetic, benzoic, chloroacetic, trichloroacetic) and with phenol dissolved in *n*-hexane, fluorobenzene, chlorobenzene, benzene, toluene, and *p*-xylene.

Thus, hydrogen bonding to a relatively weak aromatic molecule or the "permanent dipole–induced dipole" interaction (*n*-hexane) results in a band shift but no splitting, even in the case of such a strong acid as CF_3COOH.

OH Groups on SiO_2

Surface OH groups on SiO_2 were chosen as another example of homogeneous OH groups. According to Fink and Plotzki (*18*) singular (terminal) Si–OH and geminal  $\mathrm{Si}{<}^{\mathrm{OH}}_{\mathrm{OH}}$ hydroxyls exist on the SiO_2 surface. Geminal OH groups are more sensitive to dehydroxylation, and SiO_2 activated at high enough temperatures contains only one kind of surface OH group, viz., singular Si–OH groups.

In our study only one narrow band of singular Si–OH groups (3741 cm^{-1}) is present in the spectrum of SiO_2 activated at 1070 K. This band shifts to lower frequencies on the adsorption of *n*-hexane, fluorobenzene, chlorobenzene, benzene, toluene, *p*-xy-

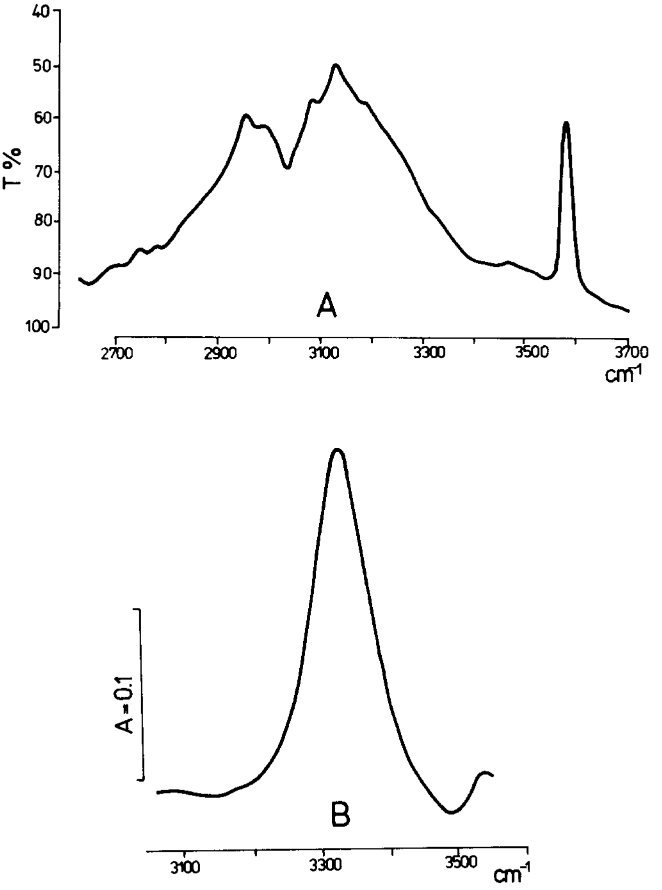


FIG. 1. OH groups in trifluoroacetic acid. (A) free OH groups and OH dimers in gaseous CF_3COOH. (B) OH groups forming a hydrogen bond with toluene molecules (spectrum of CF_3COOH dissolved in toluene minus spectrum of toluene).

lene, and ethene; the shifted band is always symmetric and no splitting is observed. The effect of *p*-xylene adsorption is presented as an example (Fig. 2). It should be noted that a symmetric OH band was also observed in the case of the hydrogen bonding of Si–OH to acetonitrile (*20*).

Thus, silica hydroxyls behave similarly to the previously described organic acids. It would therefore not be unreasonable to expect a single OH band in zeolites if hydroxyls were homogeneous.

3609 cm^{-1} OH Groups in NaH-ZSM-5 Zeolite

Two distinct OH bands exist in the spectrum of NaH-ZSM-5 zeoilite, namely, bands at 3738 cm^{-1} (Si–OH) and 3609 cm^{-1} (Si–OH–Al) (Fig. 3). Adsorption of *n*-hexane, fluorobenzene, chlorobenzene, benzene, toluene, or ethene results in a shift of the 3609 cm^{-1} band to lower frequencies. In all cases, the shifted band is asymmetric and split into several maxima. Figure 3 shows the shifted band in the case of benzene adsorption.

A computer band deconvolution was done (Fig. 4). Despite the uncertainty of such a procedure (especially in the case of strongly overlapping bands) the resulting bands correspond closely to the local maxima visible in the undeconvoluted spectrum.

Experiments described in previous sec-

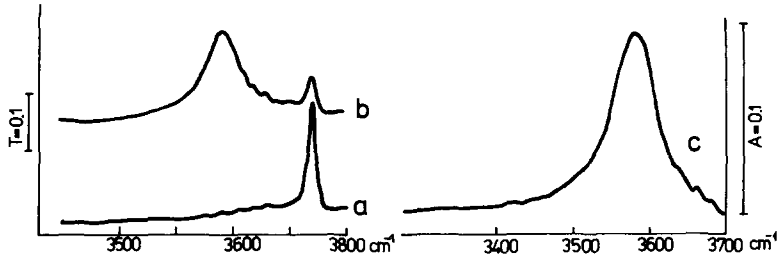


FIG. 2. OH groups on SiO_2. (a) activated SiO_2. (b) *p*-Xylene adsorbed on SiO_2. (c) spectrum of OH groups forming a hydrogen bond with *p*-xylene (spectrum b minus spectrum a).

tions show that the interaction of homogeneous OH groups with the adsorbates studied results in a single and symmetric band. The observed splitting of the OH band in the case of NaH-ZSM-5 zeolite can therefore be attributed either to the heterogeneity of OH groups or to the presence of "nonequivalent" adsorbate molecules in the zeolitic channels, be it for electronic or geometric reasons. If the former hypothesis is valid, the Bellamy–Hallam–Williams (BHW) relation (*19*) should hold; otherwise, the observed splitting is due to other reasons. The BHW equation is a linear correlation between the values of relative frequency shifts ($\Delta\nu/\nu_0$) of two acids R'OH and ROH (one of them is considered a "standard") in the same series of solvents

$$\left(\frac{\Delta\nu}{\nu_0}\right)_{\mathrm{R'OH\cdots B}} = a + b\left(\frac{\Delta\nu}{\nu_0}\right)_{\mathrm{ROH\cdots B}}$$

where ν_0 is the frequency of free OH

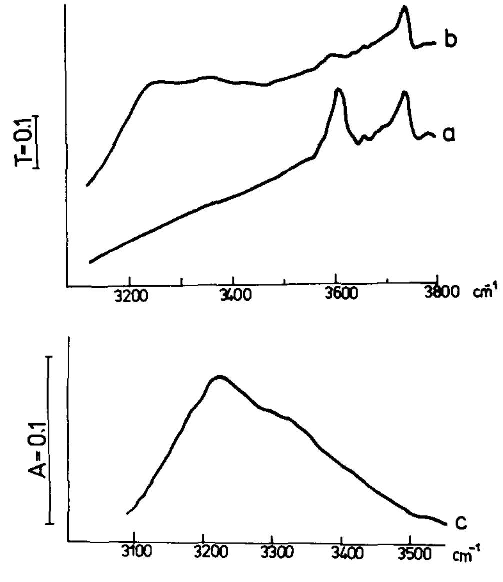


FIG. 3. OH groups in NaH-ZSM-5 zeolite. (a) activated NaH-ZSM-5. (b) benzene adsorbed on the zeolite. (c) spectrum of OH groups forming a hydrogen bond with benzene (spectrum b minus spectrum a).

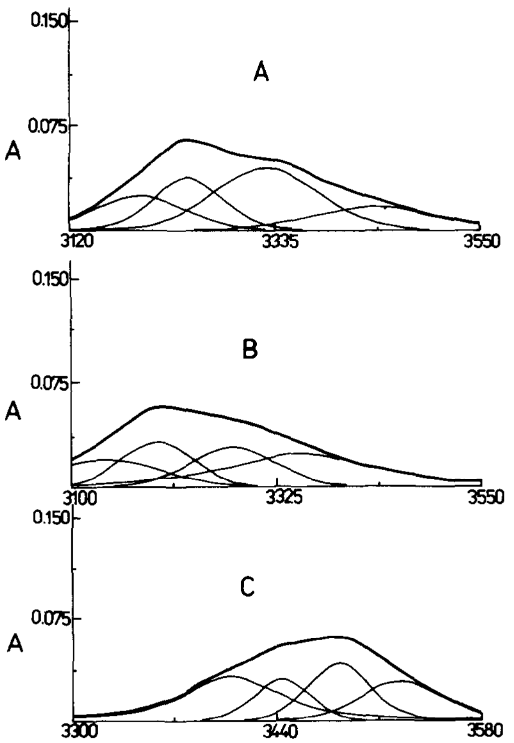


FIG. 4. The IR band of OH groups in NaH-ZSM-5 zeolite after adsorption of benzene (A), toluene (B), and *n*-hexane (C), divided into four submaxima.

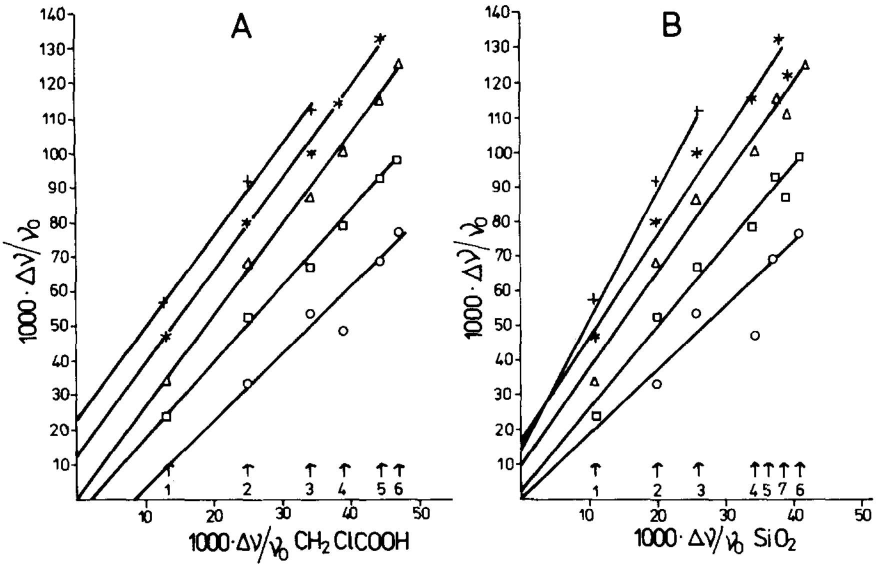


FIG. 5. Bellamy–Hallam–Williams (BHW) diagrams of OH (1, ○), OH (2, □), OH (3, △), OH (4, *) and OH (5, +) with chloroacetic acid (A) and SiO_2 (B) as "standards." Adsorbates: (1) *n*-hexane, (2) fluorobenzene, (3) chlorobenzene, (4) benzene, (5) toluene, (6) *p*-xylene, (7) ethene.

groups. Such correlations were observed in numerous cases, for example, in organic acids, alcohols, and phenols (*19–22*) and also in surface OH groups on SiO_2, B_2O_3, MgO, HX, and HY zeolites (*20, 21, 23, 24*).

The BHW diagrams were plotted for all maxima of OH groups in NaH-ZSM-5 zeolite with different adsorbates using Si–OH, phenol, and acetic, benzoic, chloroacetic, trichloroacetic, and trifluoroacetic acids as standards. All the plots are linear. Correlations for the chloroacetic acid and Si–OH standards are shown in Fig. 5.

The parameters of BHW plots, i.e., correlation coefficient (*c*), intercept (*a*), and slope (*b*), are presented in Table 2. With the exception of the band of lowest Δν, which is the most difficult to separate, all other correlation coefficients were better than 0.95. The best correlation coefficients (higher than 0.99) were found with the

TABLE 2

Correlation Coefficients (*c*), Intercepts (*a*), and Slopes (*b*) of BHW Diagrams for Five Submaxima of OH Groups in NaH-ZSM-5 Zeolite with Various "Standards"

	OH(1)			OH(2)			OH(3)			OH(4)			OH(5)		
	c	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*
Phenol	0.872	1	2.25	0.981	0	3.14	0.979	6	3.74	0.978	17	3.88	0.962	24	4.00
Acetic acid	0.825	6	1.70	0.974	1	2.55	0.972	8	3.06	0.969	19	3.11	0.975	17	3.93
Benzoic acid	0.760	15	1.28	0.956	12	2.04	0.954	20	2.45	0.949	33	2.43	0.963	34	3.00
Chloroacetic acid	0.930	−14	1.83	0.998	−4	2.16	0.997	1	2.59	0.998	12	2.67	0.998	22	2.68
Trichloroacetic acid	0.937	1.15	1.85	0.993	0	1.52	0.991	6	1.82	0.993	18	1.84	0.993	28	1.84
Trifluoroacetic acid	0.911	−9	1.20	0.993	0	1.45	0.993	5	1.74	0.992	17	1.77	0.994	27	1.75
SiO_2	0.873	−1	1.79	0.983	0	2.42	0.986	5	2.93	0.978	16	3.00	0.998	9	4.00

strongest of the standard acids, i.e., chloroacetic, trichloroacetic, and trifluoroacetic acids, the strength of which is the closest to that of zeolitic OH groups.

In our study molecules of various chemical character, and of various molecular symmetry and dimensions, were used as adsorbates. In the case of *n*-hexane, "permanent dipole-induced dipole" interaction takes place, whereas ethene forms hydrogen bonds through the π electrons of the double bond and aromatic hydrocarbons through the π electrons of the aromatic ring. Despite the great variety of adsorbates, the BHW relation is well obeyed. The hypothesized heterogeneity of the 3609 cm^{-1} OH groups in NaH-ZSM-5 zeolite is confirmed.

We conclude that at least five kinds of OH group [OH(1)–OH(5)] exist in NaH-ZSM-5 zeolite. Not all maxima, however, can be observed in all the spectra, due to overlap of the most extremely situated bands with either the C–H stretching bands (2900–3100 cm^{-1}) or the unshifted 3609 cm^{-1} OH band (always seen as a negative peak in the difference spectrum).

Several relations were proposed to express the slopes *b* of the BHW plots in terms of the parameters characterizing the acid strength of OH groups such as pK_a (*20*) or PA (proton affinity, i.e., the enthalpy change of the process $AH = A^- + H^+$) (*23*). We decided to correlate *b* with the PA values. In Fig. 6, log *b* is plotted as a function of PA for organic acids, phenol, and ethanol. The *b* values were taken from the present study and the PA values, from Refs. (25, 26). The correlation is linear and the following equation was derived:

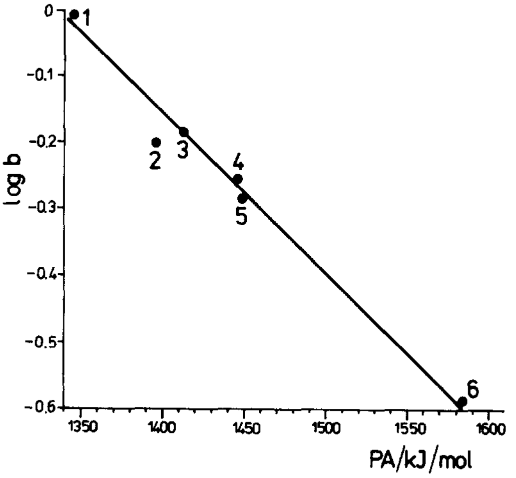


FIG. 6. Log *b* (where *b* is the slope of BHW diagrams) of acids as a function of their PA. (1) Trifluoroacetic acid, (2) chloroacetic acid, (3) benzoic acid, (4) acetic acid, (5) phenol, (6) ethanol.

$$PA = PA\ (\text{standard}) - 448 \cdot \log b.$$

An analogous equation with almost the same value of slope (442 kJ mol^{-1}) was proposed by Paukshtis and Yurchenko (*23*). From our equation the PA values for the five kinds of OH group in NaH-ZSM-5 zeolite were calculated using various standards. The results are presented in Table 3.

TABLE 3

PA Values toward Various Standards of OH Groups in ZSM-5 Zeolites

Standard	PA (kJ mol^{-1})				
	OH(1)	OH(2)	OH(3)	OH(4)	OH(5)
Phenol	1290	1225	1190	1184	1178
Acetic acid	1342	1264	1228	1225	1179
Benzoic acid	1364	1274	1238	1240	1190
Chloroacetic acid	1276	1244	1209	1203	1202
Trifluoroacetic acid	1309	1273	1237	1234	1236
Average	1316 ± 16	1256 ± 9	1220 ± 10	1217 ± 10	1197 ± 9

Again, the highest uncertainty is observed with OH(1). In all other cases the standard deviations of PA values are comparable with those of standard acids used (*25, 26*).

For a better understanding of the acidity differences studied, it is worth noticing that the difference between the weakest OH(1) group and the strongest OH(5) group ($\Delta PA = 119$ kJ mol^{-1}) is comparable with that of acetic and trifluoroacetic acids ($\Delta PA = 101$ kJ mol^{-1}). On the other hand, the OH(3) and OH(4) groups are characterized by the same approximate PA values but differ in the intercept values in BHW diagrams (Tables 2 and 3). It should be noted that all five kinds of OH group have the same 3609 cm^{-1} IR band if not affected with adsorbed molecules. A similar situation was also observed in carboxylic acids (Table 1).

Our conclusion about the heterogeneity of OH groups in NaH-ZSM-5 zeolite is corroborated by the observations of Védrine *et al.* (*8, 9*) who reported a decrease of the adsorption heat of ammonia with the amount of adsorbed base. The heterogeneity of OH groups was also suggested by Jacobs and Balmoos (*27*) who observed that the 3610 cm^{-1} band was twice as broad in NaH-ZSM-5 as in NaHY. On the other hand, Haag *et al.* (*28*) claim that the catalytically active sites in NaH-ZSM-5 are homogeneous. We note that their conclusion was based on the linear increase in catalytic activity with the amount of tetrahedral Al. However, according to Post and van Hooff (*29*), a threshold level for acid strength exists above which the catalytic activity of the zeolite does not depend on the strength of acid sites.

The origin of the heterogeneity of the 3609 cm^{-1} OH groups deserves discussion. Two explanations can be proposed. The first assumes a nonhomogeneous Al distribution within the zeolite and the presence of OH groups with different numbers of Al atoms in the close vicinity and therefore having various acid strengths (*7*). Nonhomogeneity of the Al distribution in ZSM-5 crystals has indeed been reported (*30, 31*).

Another explanation, which seems more plausible, assumes a dependence of the acid strength of zeolitic OH groups on the Al–O and Si–O bond lengths and on Si–O–Al bond angles. Beran (*32*), using the CNDO/2 method, calculated the OH dissociation energies in the $(HO)_3SiOHAl(OH)_3$ cluster and demonstrated that these values decrease with the decrease in Si–O and Al–O bond lengths and increase with the Al–O–Si angle. Olson *et al.* (*33*) found the T–O distances in ZSM-5 zeolite to be within the range 0.152–0.167 nm and the T–O–T angles to be in the range 140–177°C. According to Beran's calculations these variations should imply a variation of OH dissociation energies over 70 kJ mol^{-1}, which is comparable with the results obtained in our study (Table 3).

CONCLUSIONS

A symmetric and nonsplit IR band is observed when homogeneous OH groups (in organic acids, phenol, and SiO_2) engage in hydrogen bonding with aromatic compounds or interact with *n*-hexane molecules.

The IR band of OH groups in NaH-ZSM-5 zeolite which interact with the above molecules is asymmetric and split into several maxima. For all of these maxima the Bellamy–Hallam–Williams relation is obeyed, suggesting that they represent OH groups of various acid strength. The PA values of all five kinds of OH group were calculated.

Two possible reasons for the heterogeneity of OH groups in NaH-ZSM-5 zeolite are discussed. One attributes it to the nonhomogeneity of Al distribution and the other to various T–O bond lengths and various T–O–T bond angles. The latter seems to be more plausible.

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