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Heterogeneity of OH Groups in Faujasites Studied by IR Spectroscopy

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Heterogeneity of OH groups in faujasites was studied by analysis of the IR absorption band of free hydroxyls and hydroxyls engaged in hydrogen-bonding with chlorobenzene. The Si–O_1H–Al groups were found to be homogeneous in NaHX zeolite (Si/Al = 1.06) and heterogeneous in NaHY zeolite (Si/Al = 2.56). Experiments of pyridine sorption and desorption have shown that the more acidic hydroxyls desorb pyridine at higher temperatures than the less acidic hydroxyls. The IR spectroscopic results agree well with previously published ^{29}Si MAS NMR results. Only one Si(4Al) signal is present in the NMR spectrum of X zeolite (Si/Al ≃ 1), but there are four signals (Si(3Al), Si(2Al), Si(1Al), and Si(OAl)) in Y zeolite. As Si(OAl) cannot create bridging hydroxyls, this implies three kinds of hydroxyls of various acid strengths in NaHY zeolite and one kind in NaHX, as actually observed in the present IR study. The hydroxyl groups in NaHX zeolite can be assigned to $(AlO)_3$Si–OH–Al$(SiO)_3$, and the three kinds of hydroxyls in NaHY to $(AlO)_2(SiO)$Si–OH–Al$(SiO)_3$, $(AlO)(SiO)_2$Si–OH–Al$(SiO)_3$, and $(SiO)_3$Si–OH—Al$(SiO)_3$, respectively. The elimination of a small amount of the most acidic S–O_1H–Al by pyridine significantly reduces the calalytic activity of NaHY zeolite in butene-1 isomerization.

INTRODUCTION

Bridging hydroxyls Si–O_1H–Al projecting into supercavities are active sites in many reactions catalyzed by faujasites. Their acid strength is an important parameter, characterizing the catalytic activity of zeolites. This paper deals with the problem of heterogeneity of Si–O_1H–Al groups in faujasites, i.e., the presence of hydroxyl groups of various acid strengths in a given zeolite structure.

The acid strength of bridging Si–OH–Al groups depends mostly on two factors, the "geometrical factor" and the "chemical factor." The "geometrical factor" can be understood as the Si–O and Al–O bond distances, and the Si–OH–Al bridge angle. The quantum-chemical calculations of Beran (1, 2) and Schröder *et al.* (3) have evidenced the dependence of the O–H dissociation energy and stretching frequency on bond distances and bridge angle. The "chemical factor" can be understood as the number of Al atoms in the close vicinity of Si–OH–Al groups, i.e., the *n* number in the $(AlO)_n(SiO)_{3-n}$Si–OH–Al$(SiO)_3$ formula. According to Kazansky (4, 5) the O–H dissociation energy depends strongly on the *n* number.

A hypothesis can therefore be formulated to the effect that *homogeneous* Si–OH–Al groups (all of the same acid strength) would exist in zeolites in which all the groups have the same Si–O and Al–O bond distances, the same Si–OH–Al bridge angle, and also the same number of Al atoms in the close vicinity of the OH group (the same *n* number). On the other hand, *heterogeneous* OH groups would be expected in zeolites in which there are Si–OH–Al groups of various Si–O or Al–O bond distances, or different bridge angle, or having various numbers of Al atoms in the close vicinity (*n* number different for various hydroxyls).

A previous study (6, 7) concerned NaHZSM-5 zeolite in which the heterogeneity of bridging hydroxyls was due to geometric reasons (different Si–O and Al–O distances, and Si–OH–Al bridge angle). Now our attention is focused on faujasites in which the heterogeneity of Si–O_1H–Al hydroxyls may be due to chemical reasons. All T-atoms in faujasites are crystallographically equivalent and therefore all Si–O_1H–Al groups have the same geometry, but there may be Si–O_1H–Al hydroxyls of various numbers of Al atoms in close vicinity (various *n* numbers). The situation is different in Zeolite X and in zeolite Y. In the case of X zeolites in which Si/Al ≃ 1, all Si–OH–Al hydroxyls have 3 Al atoms in close vicinity ($n = 3$ in $(AlO)_n(SiO)_{3-n}$Si–OH–Al$(SiO)_3$). There is only one signal of Si(4Al) in the ^{29}Si MAS NMR spectrum (8), Si–O_1H–Al groups are therefore expected to be homogeneous. In Y zeolites (Si/Al ≃ 2.5) the MAS NMR spectrum (8) shows four ^{29}Si signals: Si(OAl), Si(1Al), Si(2Al), and Si(3Al). As Si(OAl) cannot create bridging hydroxyls, three kinds of Si–O_1H–Al groups of various acid strengths

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are expected in NaHY zeolites (n = 0, 1, 2 in $(AlO)_n(SiO)_{3-n}Si\text{–}OH\text{–}Al(SiO)_3$).

The goal of this study was to verify the hypothesis that $Si\text{–}O_1H\text{–}Al$ groups in NaHX zeolite are homogeneous and that in NaHY zeolite they are heterogeneous. Heterogeneity of OH groups in faujasites was studied by IR spectroscopy by the analysis of bands of free OH groups and OH groups engaged in hydrogen-bonding (by π-electrons) with chlorobenzene molecules.

The frequency of the IR band of both free and hydrogen-bonded OH groups decreases with their acid strength (9); in the case of heterogeneous OH groups, the IR band is composed of a few submaxima corresponding to hydroxyls of given acid strength. In most cases these submaxima can be seen only after the calculation of the second derivatives of the spectra. Important information on the heterogeneity of OH groups was obtained in experiments with the adsorption of pyridine and its desorption at various temperatures. If hydroxyl groups are heterogeneous, the less acidic hydroxyls (of higher stretching frequency) will desorb pyridine at lower temperatures than the more acidic ones (of lower stretching frequency). The reappearing OH band is therefore expected to shift to lower frequency with the desorption temperature. No such effect is expected in the case of homogeneous OH groups.

The catalytic activity of NaHY zeolite in butene-1 isomerization was also studied. It was expected that in the case of heterogeneous $Si\text{–}O_1H\text{–}Al$ groups the elimination of a relatively small amount of the most acidic hydroxyls would reduce distinctly the catalytic activity.

EXPERIMENTAL

Zeolite NaX (Si/Al = 1.06) was synthesized in the Fritz-Haber-Institut in Berlin. It was transformed into an ammonium form by CH_3COONH_4 solution (pH 6–6.7) treatment at room temperature. The Na/NH_4 exchange degree was 28%. Zeolite Y (Si/Al = 2.56) was synthesized at Institute of Industrial Chemistry in Warsaw. It was transformed into an ammonium form by NH_4NO_3 solution treatment at 80°C. The exchange degree was 77%. For IR studies $NaNH_4X$ and $NaNH_4Y$ zeolites were pressed into thin wafers and activated *in situ* in the IR cell at 650 K (zeolite X) and 720 K (zeolite Y), for 1 hr.

Pyridine and chlorobenzene (POCh, Gliwice, chemical grade) and butene-1 (Fluka) were used without further purification.

IR spectra were recorded using a Bruker IFS48 PC Fourier transform spectrometer equipped with a MCT detector.

RESULTS

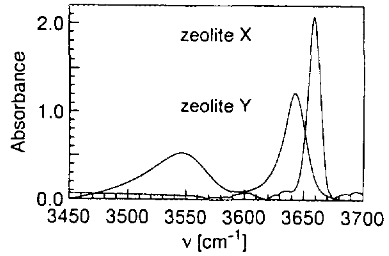

FIG. 1. The IR spectra of free $Si\text{–}O_1H\text{–}Al$ groups in NaHX and NaHY zeolite.

The spectrum of NaHX zeolite (Fig. 1) shows one distinct $Si\text{–}O_1H\text{–}Al$ band at 3660 cm^{-1}. Two bands at 3642 cm^{-1} ($Si\text{–}O_1H\text{–}Al$) and 3545 cm^{-1} ($Si\text{–}O_3H\text{–}Al$) are present in the spectrum of NaHY zeolite. The heterogeneity of the $Si\text{–}O_1H\text{–}Al$ groups was studied by analysis of the IR bands of both free and hydrogen-bonded OH groups.

Figures 2A and 2B show the spectra of $Si\text{–}O_1H\text{–}Al$ groups shifted to lower frequencies by hydrogen-bonding with chlorobenzene. In order to isolate the band of perturbed $Si\text{–}O_1H\text{–}Al$ from $Si\text{–}O_3H\text{–}Al$ (3545 cm^{-1}) and from pyridinium ions (3240 cm^{-1}), the spectra were cut in the regions 3400–3480 cm^{-1} and 3270–3450 cm^{-1} and linear

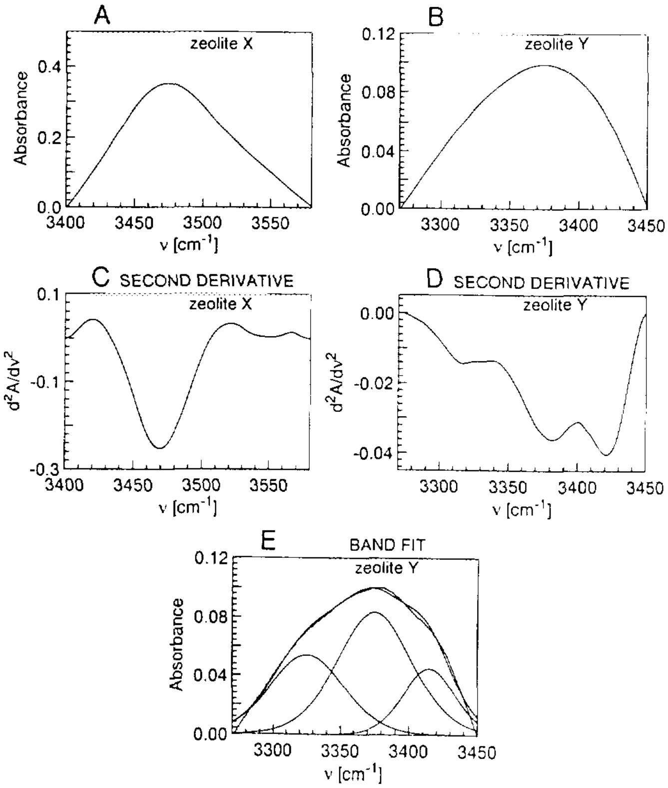

FIG. 2. The band of $Si\text{–}O_1H\text{–}Al$ groups in NaHX and in NaHY zeolites hydrogen-bonded with chlorobenzene: (A) zeolite X, (B) zeolite Y, (C) second derivative for zeolite X, (D) second derivative for zeolite Y, and (E) the band fit for zeolite Y.

baseline subtraction was done. In the case of NaHX zeolite, the shifted band is relatively narrow and not split. On the other hand, in NaHY zeolite, the shifted band is twice as broad and asymmetric, thus suggesting that it comprises several submaxima. It may be supposed that in NaHX zeolite Si-O$_1$H-Al groups are homogeneous and in NaHY heterogeneous (a few kinds of hydroxyls of various acid strengths and various $\Delta\nu$ exist). In order to improve the spectral resolution (and to see such submaxima, if they exist) the second derivative of the band of hydrogen-bonded OH groups was calculated. Before this operation the spectra were smoothed by the method of spline functions (10). The second derivative diagrams are presented in Figs. 2C and 2D. In the case of NaHX zeolite, only one band at 3478 cm^{-1} ($\Delta\nu$ = 182 cm^{-1}) is present, whereas three submaxima at 3320, 3380, and 3420 cm^{-1} exist in NaHY. These frequencies were used as input data for the band fitting procedure by using the computer program of Phita and Jones (11, 12). The results are presented in Fig. 2E. The submaxima frequencies obtained from band fit were 3326, 3378, and 3419 cm^{-1} ($\Delta\nu$ = 316, 264, and 223 cm^{-1}). The data presented in Fig. 2C–2E support the hypothesis that the Si-O$_1$H-Al groups are homogeneous in NaHX and heterogeneous in NaHY. Only one kind of hydroxyls exist in NaHX and three kinds of hydroxyls of various acid strengths in NaHY.

Further evidence that Si-O$_1$H-Al groups in NaHX zeolite are homogeneous and in NaHY are heterogeneous was obtained from experiments of pyridine sorption and desorption. Pyridine was first sorbed in zeolites at 423 K up to neutralizing all Si-O$_1$H-Al groups, and then it was desorbed step by step at increasing temperatures (603–693 K for NaHX and 668–798 K for NaHY) for 30 min. The IR spectra recorded at room temperature after each desorption step are presented in Figs. 3A and 3B. Chlorobenzene was subsequently sorbed in zeolites with preadsorbed pyridine. The IR spectra of Si-O$_1$H-Al groups hydrogen-bonded with chlorobenzene are presented in Figs. 3B and 3D. In the case of NaHX the band frequencies of free and hydrogen-bonded hydroxyls are practically independent of the desorption temperature, thus indicating that hydroxyls releasing pyridine at lower temperatures are of the same frequency (and the same acid strength) as those releasing pyridine at higher temperatures. This means that the Si-O$_1$H-Al groups in NaHX zeolite are homogeneous. Very small band shifts (2 and 10 cm^{-1} respectively, Figs. 3A and 3C) can be explained by the fact that pyridine desorption decomposes PyH$^+$ ions and replaces them by protons which increase the acid strength of neighbouring hydroxyls. Larger shifts are observed in the case of NaHY zeolite (13 and 25 cm^{-1} respectively, Fig. 3C and 3D), indicating that Si-O$_1$H-Al groups are heterogeneous: less acidic hydroxyls (of higher stretching frequencies) release pyridine at lower temperature than more acidic ones. This can be seen better in Fig. 4, in which the fit of the bands of hydrogen-bonded hydroxyls in the zeolites with pyridine is presented. The intensity ratio of submaxima corresponding to the most acidic hydroxyls (3326 cm^{-1}) and the less acidic ones (3419 cm^{-1}) increases with the temperature of pyridine desorption: it is the highest in the case of activated zeolite, without pyridine sorption.

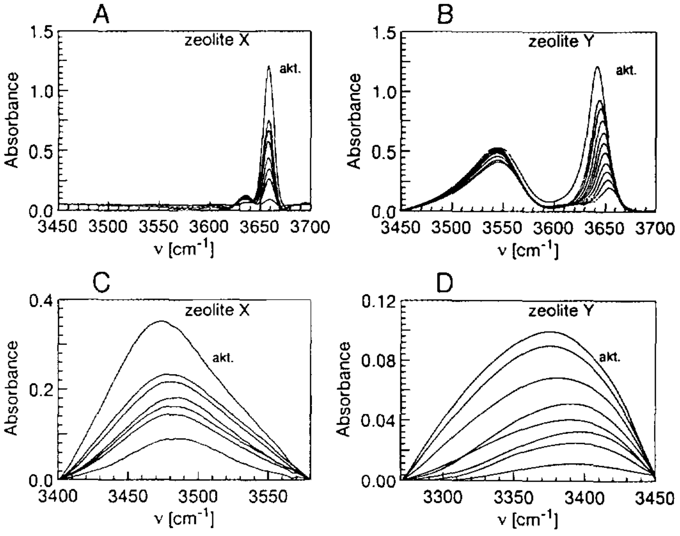

FIG. 3. The IR spectra of Si-O$_1$H-Al groups in NaHX and NaHY zeolite: (A) free OH groups in zeolite X, spectrum of activated zeolite and spectra recorded after pyridine sorption and desorption at 603, 638, 648, 658, 673, 683, and 693 K; (B) free OH groups in zeolite Y, spectrum of activated zeolite and spectra recorded after pyridine sorption and desorption at 668, 683, 693, 703, 718, 728, 748, 758, 788, and 798 K; (C) OH groups in NaHX zeolite hydrogen-bonded with chlorobenzene, chlorobenzene sorbed in activated zeolite, and after pyridine sorption and subsequent desorption at 638, 648, 658, 673, 683, and 693 K; (D) OH groups in NaHY zeolite hydrogen-bonded with chlorobenzene, chlorobenzene sorbed in activated zeolite, and after pyridine sorption and subsequent desorption at 693, 703, 728, 748, 758, 788, and 798 K.

The results of these experiments of pyridine sorption and desorption agree well with the conclusion that Si-O$_1$H-Al groups in NaHX zeolite are homogeneous and in NaHY heterogeneous.

The catalytic activity of NaHY zeolite in butene-1 isomerization was studied. Pyridine was first sorbed in the zeolite at 423 K up to neutralizing all Si-O$_1$H-Al groups and then desorbed step by step at increasing temperatures. Butene-1 was sorbed in the zeolite at 293 K and the rate of isomerization was studied by following the loss of intensity of the 1631-cm^{-1} winyl group band in the butene-1 molecules. The isomerization was found to be a first-order reaction. The rate constants are presented in Fig. 5 as a function of the percentage of Si-O$_1$H-Al replaced by pyridinium ions. The elimination of 10% of

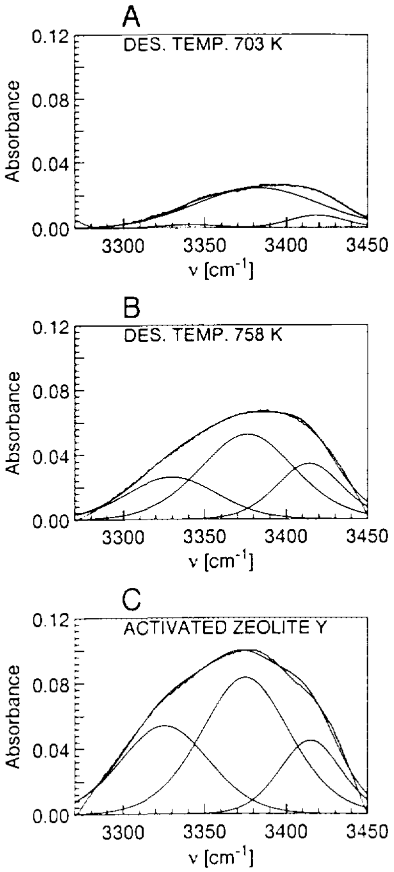

FIG. 4. The band fit for the band of Si–O_1H–Al groups in NaHY zeolite hydrogen-bonded with chlorobenzene: (A, B) chlorobenzene sorbed upon pyridine sorption and subsequent desorption at 703 and 758 K; (C) activated zeolite.

Si–O_1H–Al reduced the catalytic activity by 70%, and elimination of 46% of Si–O_1H–Al reduces the activity by 95%.

DISCUSSION

The results show that the heterogeneity of the OH groups in faujasites can be studied by analysis of the IR band of free hydroxyls and hydroxyls engaged in hydrogen-bonding with chlorobenzene. Chlorobenzene was used because of the appropriate values of frequency shifts thereby obtained. If the frequency shift is too small, the shifted band would overlap the 3545-cm^{-1} Si–O_3H–Al band in NaHY zeolite; if it is too large, the shifted band would overlap the 3240 cm^{-1} band of PyH$^+$ ions. The results obtained in this study support the hypothesis that Si–O_1H–Al groups in NaHX zeolite are homogeneous and in NaHY are heterogeneous (three kinds of hydroxyls of various acid strengths were found). The elimination of a small amount of the most acidic Si–O_1H–Al reduces distinctly the catalytic activity in butene-1 isomerization.

Although no systemic studies of the problem of heterogeneity of hydroxyl groups in faujasites have been undertaken before, some results obtained by other authors do also suggest that Si–O_1H–Al groups in HY zeolites are heterogeneous. Dzwigaj *et al.* (13) as well as Dombrowski *et al.* (14) reported the existence of several submaxima in the 3640-cm^{-1} band. Kubelkova *et al.* (15) observed two submaxima in the band of OH groups in HY zeolite interacting by hydrogen-bonding with CO molecules (at low coverages CO molecules reacted preferentially with more acidic hydroxyls). Lombardo *et al.* (16) also observed the poisoning of the catalytic activity of NaHY zeolite in neopentane cracking by small doses of ammonia. This results agrees well with our data presented in Fig. 5.

It may be supposed that the heterogeneity of the OH groups in NaHY zeolite observed in our study is due to the presence of $(AlO)_n(SiO)_{3-n}$Si–OH–Al$(SiO)_3$ groups of different n number. The ^{29}Si MAS NMR studies (8, 17) have shown that there are Si atoms of various numbers of Al in the second coordination sphere: (Si(OAl), Si(1Al), Si(2Al), Si(3Al)). As Si(OAl) cannot create bridging hydroxyls, three kinds of bridging OH groups are expected in HY zeolites. The results obtained in our study have confirmed that three kinds of Si–O_1H–Al groups of various acid strength do indeed exist. In the case of NaHX zeolite there is only one kind of hydroxyls, which is in agreement with the MAS NMR results (8) (only one Si(4Al) signal). The hydroxyls in NaHX zeolite (where the frequency shift accompanying hydrogen-bonding with chlorobenzene is $\Delta\nu_{\text{chlorob}}$ = 182 cm^{-1}), which will be called OH(1), can therefore be assigned to $(AlO)_3$Si–OH–Al$(SiO)_3$ (n = 3). Three kinds of hydroxyls on NaHY zeolite ($\Delta\nu_{\text{chlorob}}$ = 223, 264, and 316 cm^{-1}),

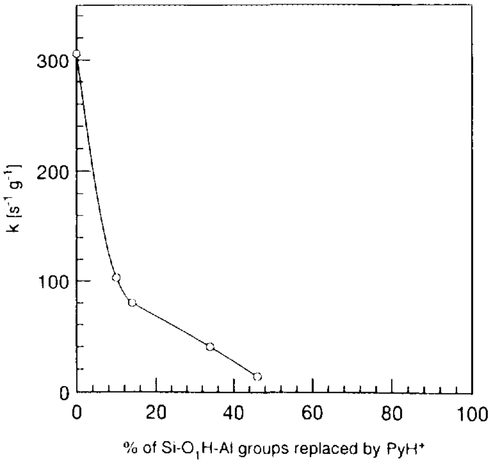

FIG. 5. The rate constant of butene-1 isomerization as a function of the percentage of Si–O_1H–Al groups in NaHY zeolite replaced by pyridinium ions (PyH$^+$).

which will be called OH(2), OH(3), and OH(4), can be assigned to $(AlO)_2(SiO)Si-OH-Al(SiO)_3$, $(AlO)(SiO)_2Si-OH-Al(SiO)_3$, and $(SiO)_3Si-OH-Al(SiO)_3$ (n = 2, 1, and 0), respectively.

The MAS NMR data (8, 17) have shown that the Si(4Al) signal, the only signal in X zeolite, is absent in the spectra of Y zeolites (Si/Al = 2.5). This implies, that OH(1) groups (the only groups in NaHX zeolite) should be absent in NaHY zeolite. The results presented in Fig. 1 show that this is indeed the case. The 3660-cm^{-1} band characteristic of free hydroxyls in NaHX zeolite is absent in the spectrum of NaHY.

Another interesting comparison between MAS NMR and IR data concerns the relative intensities of NMR signals and IR bands. According to the results obtained by Engelhardt *et al.* (17, 18), the ratio of the signal intensities of Si(3Al) : Si(2Al) : Si(1Al) in a Y zeolite (Si/Al = 2.5) is 1 : 3.5 : 2.7. The ratio of the amounts of OH(2) : OH(3) : OH(4) hydroxyls should be the same. The ratio of the integrated intensities of submaxima in the IR spectrum of OH groups in NaHY zeolite (Si/Al = 2.56) interacting with chlorobenzene and corresponding to OH(2), OH(3), and OH(4) groups is 1 : 2.7 : 1.7 (Fig. 2E). Assuming that the extinction coefficients of these IR bands are comparable, these values represent the ratio of concentrations of OH(2), OH(3), and OH(4) groups, which agrees with the NMR data. A small difference between the NMR and IR results can be partly explained by a nonrandom distribution of protons between O(2), O(3), and O(4).

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