JOURNAL OF CATALYSIS **102**, 43–51 (1986)

Infrared Spectroscopic Studies of Acid Properties of NaHZSM-5 Zeolites

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Received April 10, 1984; revised October 21, 1985

Acid properties of NaHZSM-5 zeolites of various exchange degrees were studied by quantitative infrared (IR) studies of pyridine adsorption. It has been verified that pyridine may be used as adsorbate for such studies. Two series of NaHZSM-5 zeolites were prepared by exchange in HCl and NH_4NO_3 solutions. Two kinds of Brønsted acid sites were detected in NaHZSM-5 zeolites, OH groups vibrating at 3609 cm^{-1} being strong acid sites and other protonic sites of lower acidity. The concentrations of these two kinds of Brønsted site and also of Lewis acid sites were determined as a function of exchange degree and also of mode of preparation. It has been found that first protons introduced into zeolite form weak Brønsted acid sites and a small amount of 3609-cm^{-1} OH groups. The amount of weak acid sites attains a constant value after the exchange of 30–40% of Na^+ ions and the next-introduced protons form 3609-cm^{-1} OH groups. The mode of introduction of protons do not influence either the sequence of sites formation or the proportion of strong and weak acid sites. The amounts of acid sites determined by IR spectroscopy were found to be equal to the amounts of protons introduced into zeolites by the ion exchange, thus indicating that the introduction of protons into the zeolite do not "acidify" weaker sites preexisting in the zeolite before ion exchange. The protonic acid sites in NaHZSM-5 zeolite are resistant to dehydroxylation (the amount of Lewis acid sites is low), which may be due to the high Si/Al ratio of zeolites studied in the present research. © 1986 Academic Press, Inc.

INTRODUCTION

ZSM-5 zeolites attract much attention at the present time because of their interesting catalytic properties and great resistance to deactivation. These properties originate from a specific pore system in which shape selectivity is observed (*1–4*) and also from a particular type of acidity (low concentration and high acid strength of sites).

The acidic properties of ZSM-5 type zeolites have been studied using various methods, the most important of which are microcalorimetry (*5–10*), TPD (*11–15*), and IR spectroscopy (*5, 6, 12, 16–21*).

Microcalorimetric and TPD studies of NH_3 adsorption and desorption enabled estimation of the concentration and the strength of acid sites. From the results of microcalorimetric studies it was possible to compare the heats of adsorption of NH_3 on different types of zeolites (*8, 13–15*), ZSM-5 zeolites of various Al content and ZSM-5 zeolites after various treatments (*6, 7, 9, 10*). Conclusions about the heterogeneity of the acid sites could be also be drawn from microcalorimetric data (*6, 9*).

The information obtained in microcalorimetric and TPD studies concern however the total content of acid sites of Brønsted and Lewis type without distinguishing between them. The mechanisms of reactions catalyzed by these two kinds of sites are different and it is important to determine their concentration and to study the properties of Brønsted and Lewis acid sites separately. This may be done with help of IR spectroscopy.

IR studies of the acidic properties of ZSM-5 zeolites have been described in various papers (*5, 6, 12, 16–21*). The most important results may be summarized as follows. The hydrogen form of ZSM-5 zeolites contain both Brønsted and Lewis acid sites.

0021-9517/86 $3.00

Their concentrations were found to be comparable. Calcination of these zeolites results in dehydroxylation which is accompanied by a decrease of the concentration of Brønsted acid sites and formation of Lewis acid sites. Two distinct bands of OH groups appear in the IR spectrum of NaHZSM-5 zeolites at 3605 and 3720 cm^{-1}. The latter band is also present in NaZSM-5 zeolites and was assigned to an extrazeolitic material (*17*). The band at 3605 cm^{-1} characterizes strong Brønsted acid sites. The intensity of this band increases linearly with the Al content. Its extinction coefficient and the half-width are higher than those in the case of HY zeolite suggesting the high acid strength and heterogeneity of 3605-cm^{-1} OH groups in ZSM-5 zeolites. This latter conclusion is in accordance with the results of microcalorimetric studies.

Practically all the above-described IR studies of ZSM-5 zeolites are qualitative. The concentrations of Brønsted and Lewis acid sites were determined in the case of only one ZSM-5 zeolite (*18*). In the present research systematic quantitative IR studies were undertaken in order to determine the concentrations of Brønsted and Lewis acid sites in NaHZSM-5 zeolites of various exchange degrees. It was considered interesting to study the acid properties of these zeolites as a function of the exchange degrees and also as a function of the mode of preparation (acidification by NH_4NO_3 and HCl solutions). The acid properties of NaZSM-5 of various compositions are described in a previous paper (*22*). It has been found that the concentrations of acid sites in NaZSM-5 zeolites depend on their composition, being higher in zeolites with higher sodium deficit than in zeolites with low sodium deficit.

EXPERIMENTAL

NaHZSM-5 zeolites were obtained from a parent sodium form ("Utrazet") sample prepared at the Institute of Industrial Chemistry (Warsaw), the composition of which was $Na_{1.7}H_{0.3}(AlO_2)_2(SiO_2)_{94}$ (Si/Al ratio = 47, and Na/Al = 0.85).

Two series of hydrogen forms NaHZSM zeolites were prepared, one by the exchange of Na$^+$ into NH_4^+ ions in NH_4NO_3 solution and another by the exchange in HCl solutions. Various exchange degrees were obtained by using various concentrations of NH_4NO_3 and HCl solutions. The highest concentrations of these solutions were 1 *M* and 0.5 *M*, respectively. After the ionic exchange, the zeolites were washed and dried at 390 K. In order to attain high homogeneity and high dispersion, the samples were ground in a colloid mill.

In order to calculate the exchange degrees, the zeolites were dissolved in HF solution and the sodium content was determined by atomic absorption. The degree of cation exchange was calculated as the percent of Na$^+$ ions substituted by H$^+$ or NH_4^+ during the ionic exchange procedure. The parent non-exchanged NaZSM-5 zeolite is denoted as 0% exchanged despite the fact that it contains some amount of H species (0.3 per unit cell). These H species equilibrating the Na deficit are not considered to have the same properties as protons introduced during the ionic exchange. The zeolites obtained by the HCl treatment were denoted as: HZ-41, HZ-81, HZ-88 (exchange degree, 41, 81, 88%, respectively), and the zeolites obtained by the NH_4NO_3 treatment and further decomposition of NH_4^+ ions as: NZ-31, NZ-43, and NZ-83 (exchange degrees 31, 43, and 83, respectively).

For the IR spectroscopic studies the zeolites were pressed into thin wafers (3–10 mg/cm^2) containing 11–25 mg of material. The wafers inserted into IR cell were pretreated *in vacuo* at 723 K for 1 h. Such activation conditions were chosen on the basis of IR experiments described in the next section. Under these conditions complete water desorption and decompositions of NH_4^+ ions took place without any appreciable dehydroxylation.

Pyridine (POCh Gliwice, analytical

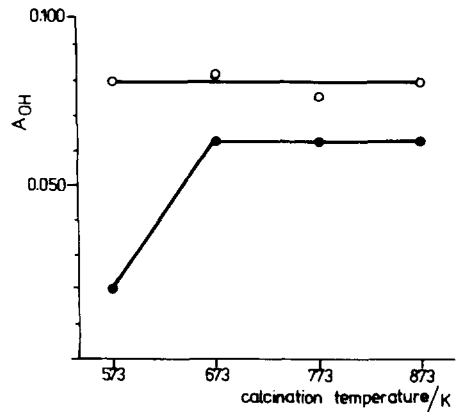

FIG. 1. The intensity of the 3609-cm^{-1} OH band as a function of activation temperature. (○) HZ-88, (●) NZ-83.

grade, was dried over KOH; NH_3 (Putawy) was purified by a bulb-to-bulb distillation. IR spectra were recorded with a Specord 75 IR spectrometer. The accumulation and subtraction of spectra were done with a KSR 4100 minicomputer working on-line with the spectrometer.

RESULTS

OH Groups

Two distinct OH bands are present in the spectra of NaHZSM-5 zeolites, at 3609 cm^{-1} and at 3738 cm^{-1} (the same as in NaZSM-5). There is also a very weak band at 3670 cm^{-1}.

In order to choose the most appropriate temperature for the activation of the zeolites the wafers of HZ-88 and NZ-83 zeolites were heated in the IR cell *in vacuo* successively at 573, 673, 773, and 873 K. After each heating the sample was cooled to 443 K and the IR spectrum recorded. Figure 1 shows the plots of the intensities of the 3609-cm^{-1} OH band as a function of heating temperature. In HZ-88 zeolite the intensity of this band was constant. However, in the case of NZ-83 the intensity increased in the temperature range 573–673 K and above 673 K remained constant. Such results indicate that OH groups in NaZSM-5 zeolites are resistant to the dehydroxylation; the increase of the intensity of the OH band below 673 K in NZ-83 zeolite is due to the decomposition of NH_4^+ ions and formation of OH groups.

On the basis of these data, the temperature of 723 K was chosen as the activation temperature for all NaHZSM samples.

Figure 2 shows the plot of the intensities of the OH 3609 cm^{-1} bands (expressed per 1 g of the zeolite) in the NZ and HZ series of NaHZSM-5 zeolites as a function of the exchange degree. In both series of NaHZSM-5 zeolites, the intensities of the 3609-cm^{-1} OH band increase with the exchange degree, i.e., with the amount of protons introduced into the zeolites. This increase, however, is not linear: at lower exchange degrees the slope of the line is lower than at higher exchange.

The Determination of Brønsted Acid Sites by NH_3 Adsorption

The adsorption of NH_3 in NaHZSM-5 zeolites results in the formation of NH_4^+ ions, the bands of which appear in the spectrum. The most characteristic band of the NH_4^+ ion is that due to asymmetric deformation at 1430 cm^{-1}. This band is best seen after the computer subtraction of the spectrum of activated zeolite from the spectrum of the zeolite with ammonia adsorbed. The extinction coefficient of the 1430-cm^{-1} band was determined by the adsorption of known portions of NH_3 on NZ-83. The value 0.069

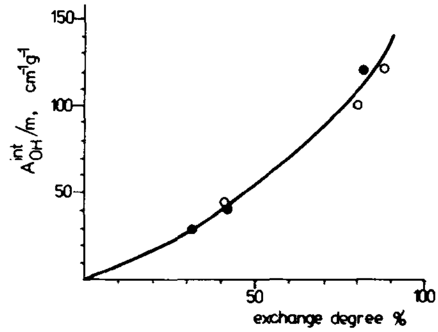

FIG. 2. The integrated intensity of the 3609-cm^{-1} OH band expressed per 1 g of zeolite (A^{int}_{OH}/m) as a function of exchange degrees. (○) HZ series, (●) NZ series.

TABLE 1

Concentrations of Brønsted Acid Sites as Determined by NH_3 and Pyridine Adsorption

Zeolites	Sites per unit cell as determined by the adsorption of	
	NH_3	Pyridine
NH-83	1.50	1.25
HZ-88	1.40	1.35

cm^2 μmol^{-1} obtained in the present investigation approximates to the value determined in the case of NaHY zeolite (0.075 cm^2 μmol^{-1} (*23*).

In order to determine the concentration of Brønsted acid sites amounts of NH_3 sufficient to neutralize all acid sites were adsorbed on HZ-88 and NZ-83. The concentrations of Brønsted acid sites were calculated from the intensity of the 1430-cm^{-1} NH_4^+ band and its extinction coefficient. The values obtained are given in Table 1. The determination of acidity based on IR studies by NH_3 adsorption is not very convenient because the bands of ammonia complexes are rather broad and diffuse; the accurate measuring of their intensity is difficult. Such a study may be better done using pyridine as adsorbate. Systematic quantitative IR studies of pyridine adsorption on NaHZSM-5 zeolites were carried out in the present research.

Pyridine Adsorption on NaHZSM-5 Zeolites

Adsorption of pyridine on NaHZSM-5 zeolites results in the appearance of IR bands characteristic of the following complexes: PyH^+ ions (1545 cm^{-1}), pyridine complex adsorbed on Lewis acid sites PyL (1455 cm^{-1}), and pyridine adsorbed on Na^+ ions $PyNa^+$ (1445 cm^{-1}). Small measured portions of pyridine were adsorbed on the zeolites at 443 K and IR spectra were recorded at the same temperature after each adsorption step. Figure 3A shows the plots of intensities of the 1545-cm^{-1} band of PyH^+ and the 3609-cm^{-1} OH band as a function of the amount of pyridine adsorbed on HZ-88 zeolite. The adsorption of the first portions of pyridine results in a linear increase in the intensity of the PyH^+ band and in a linear decrease of the 3609-cm^{-1} OH band. A weak band at 1455 cm^{-1} appears, indicating that some pyridine molecules react with Lewis acid sites. The 1445-cm^{-1} $PyNa^+$ band is absent. After the disappearance of the 3609-cm^{-1} OH band the adsorption of the next portions of pyridine results in a further increase of the PyH^+ band, indicating that some Brønsted acid sites of weaker acidity exist besides the 3609-cm^{-1} OH groups. After the neutralization of all the Brønsted acid sites the intensity at 1545 cm^{-1} attains a constant value. The adsorption of the next portions of pyridine results in the appearance of the 1445-cm^{-1} $PyNa^+$ band.

The effects observed in the course of ad-

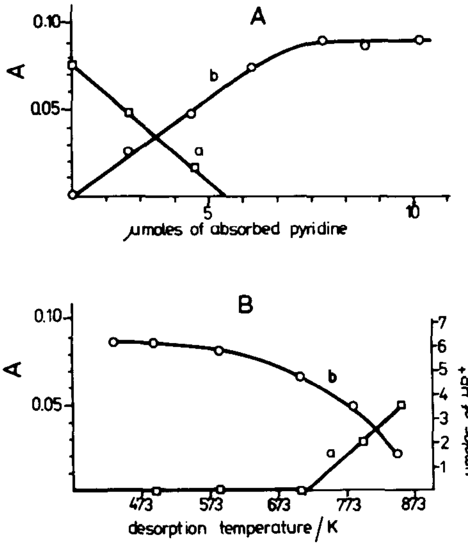

FIG. 3. (A) Adsorption of pyridine on HZ-88 zeolite: the intensities of the 3609-cm^{-1} OH band (a) and of the 1545-cm^{-1} HP_y^+ band (b) as a function of the amount of pyridine adsorbed. (B) Desorption of pyridine from HZ-88 zeolite: the intensities of the 3609-cm^{-1} OH band (a) and of the 1545-cm^{-1} HP_y^+ band (b) as a function of desorption temperature.

sorption of pyridine on other NaHZSM-5 zeolites are similar to those observed in the case of HZ-88 described above. Only in the case of zeolites of low exchange degree and high Na^+ content do the bands of $PyNa^+$ appear before the neutralization of all the Brønsted acid sites.

The stability of complexes of pyridine adsorbed on NaHZSM-5 zeolites was studied in desorption experiments. The results obtained for HZ-88 zeolite are shown in Fig. 3B. After adsorption of an excess of pyridine the cell containing the zeolite was connected with a liquid nitrogen trap and was heated to 493, 593, 703, 783, and 843 K. After each desorption step the cell was cooled to 443 K and IR spectra recorded at this temperature. The desorption of pyridine results in the decomposition of PyH^+ ions (the 1545-cm^{-1} band diminishes), but at relatively low temperatures, i.e., below 700 K, the 3609-cm^{-1} OH band does not reappear despite the decrease of the PyH^+ band. Above this temperature, the decomposition of PyH^+ ions is accompanied by the reappearing and increase in the intensity of the 3609-cm^{-1} OH band.

These results are consistent with those obtained in the adsorption experiments and confirm the fact that there are two kinds of Brønsted acid sites in NaHZSM-5 zeolites: these are the 3609-cm^{-1} OH groups which are strong acid sites and then also some other sites of lower acidity. Pyridine molecules adsorbed on the zeolite react at first with the strong acid site 3609-cm^{-1} groups and, after their neutralization, with the weaker acid sites. Desorption removes molecules from weak Brønsted acid sites at first, and molecules from 3609-cm^{-1} OH groups afterward.

Generally the stability of pyridine complexes in zeolites increases in the order $PyNa^+ < PyH^+$ (weak Brønsted acid sites) $< PyH^+$ (strong Brønsted acid sites) $<$ PyL. Such a sequence was also observed in NaHY zeolites (*23*) and is also consistent with the order of the strength of acid sites found by Michel *et al.* (*27*).

Determination of Concentration of All Brønsted and Lewis, Acid Sites

In order to determine the concentrations of all Brønsted and Lewis acid sites the portions of pyridine were adsorbed on zeolites until the bands of PyH^+ and PyL attained constant values. The concentrations of these sites were calculated from maximal intensities of PyH^+ and PyL bands and appropriate values of their extinction coefficients. The value 0.084 $cm^2\ \mu mol^{-1}$ determined for dehydroxylated Y zeolites (*24*) was taken as the extinction coefficient of the PyL band for NaHZSM-5 zeolites. The value of the extinction coefficient of the PyH^+ 1545-cm^{-1} band was calculated from the linear dependence of the intensity of this band from the concentration of pyridine molecules reacting with Brønsted acid sites. This last value was taken as the difference between the total amount of adsorbed pyridine and the amount of pyridine reacting with Lewis acid sites (calculated from the intensity of the PyL band and its extinction coefficient). The value of the extinction coefficient for PyH^+ formed in NaHZSM-5 zeolites (0.058 $cm^2\ \mu mol^{-1}$) agrees well with the value observed in the case of NaHY zeolites (0.059 $cm^2\ \mu mol^{-1}$) (*25*).

The values of the concentrations of Lewis and Brønsted acid sites (3609-cm^{-1} OH groups and weak acid sites) determined in NaHZSM-5 zeolites (NZ and HZ series) are presented in Figs. 4A and B (lines a and d). They increase with the exchange degree, i.e., with the amounts of protons introduced into the zeolite.

The parent NaZSM-5 zeolite contains also some amount of Brønsted acid sites (0.12 per unit cell) and of Lewis acid sites (0.04 per unit cell). These data are also presented in Figs. 4A and B as points at 0% of exchange).

Assuming that two protonic acid sides (OH groups) condense forming one Lewis acid site, the sum B + 2L (where B and L are the concentrations of Brønsted and

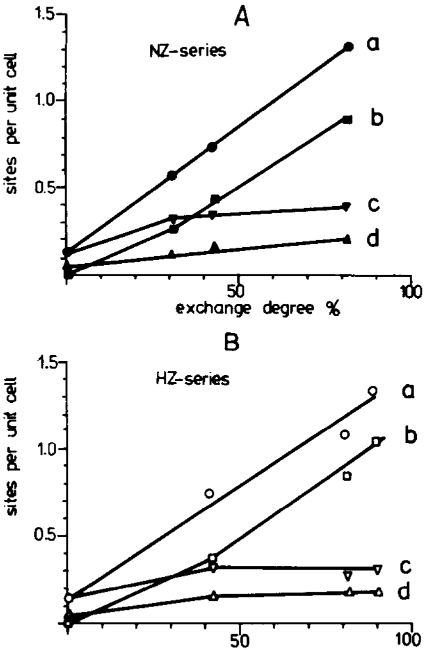

FIG. 4. The concentrations of acid sites in NaHZSM-5 zeolites as a function of exchange degree. (A) NZ series, (B) HZ series. (a All Brønsted acid sites, (b strong Brønsted acids sites (3609 cm^{-1} OH groups), (c weak Brønsted acid sites, (d Lewis acid sites.

Lewis sites, respectively) represents the hypothetical initial concentration of protonic acid sites. These values are given in Fig. 5 (open circles for HZ and full circles for the NZ series). The concentration of protons introduced into the zeolite during the ion exchange augmented by the constant value of acidity of the parent sodium zeolite is also presented in the same diagram as a function of the exchange degree (straight line). The theoretical values expressed by the line agree well with the experimental data (points).

Determination of the Concentrations of Strong and Weak Brønsted Acid Sites

As already mentioned, NaHZSM-5 zeolites contain strong Brønsted acid sites (3609-cm^{-1} OH groups), and Brønsted sites of weaker acidity. If an excess of pyridine is adsorbed on the zeolite, and then pyridine is desorbed at various temperatures, the molecules neutralizing weak acid sites desorb at relatively lower temperatures (below 700 K) without reappearance of the 3609-cm^{-1} OH band (Fig. 3B). At higher temperatures the molecules neutralizing 3609 cm^{-1} OH groups desorb and this OH band reappears in the spectrum.

The amount of PyH^+ ions decomposed before the 3609-cm^{-1} OH band begins to reappear was taken as the amount of weak Brønsted acid sites, and the remainder as the amount of strong sites (3609-cm^{-1} OH groups). The data concerning HZ-88 zeolite are presented in Fig. 3B. In this case 1.4 and 4.7 μmol of weak and strong Brønsted acid sites, respectively, were found in the sample which corresponds to 0.30 and 1.03 sites per unit cell.

The results concerning the weak and strong acidity of NaHZSM-5 zeolites are presented in Figs. 4A and B. The parent NaHZSM-5 zeolites contains only weak Brønsted acid sites. The 1545-cm^{-1} band disappears after the desorption at 700 K.

The values of the integrated extinction coefficient (IEC) of the 3609-cm^{-1} OH band of NaHZSM-5 zeolites were calculated from the intensities of these bands (Fig. 2) and their concentrations (Figs. 4A and B, lines b). The following values were obtained: 1.8 and 2.7 cm μmol^{-1} for NZ-43 and NZ-88, respectively, and 2.3, 2.8, and

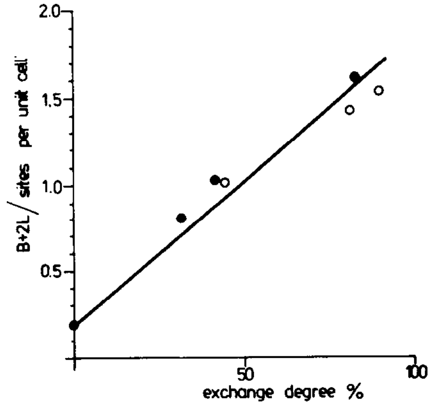

FIG. 5. B + 2L (B—concentration of Brønsted acid sites, L—concentration of Lewis acid sites) as a function of the exchange degree.

2.7 cm μmol^{-1} for HZ-41, HZ-81, and HZ-88, respectively.

DISCUSSION

In the present work a systematic study of the acidic properties of NaHZSM-5 zeolites was undertaken by quantitative IR experiments of pyridine adsorption. Pyridine has frequently been used for IR studies of the acidity of faujasite-type zeolites. In the case, however, of ZSM-5 zeolites, the diffusion of pyridine may be restricted inside the channels, and some acid sites may remain undetected; the applicability of this method must therefore be verified. For this purpose, the concentrations of Brønsted acid sites in NaHZSM-5 zeolites of high exchange degrees (NH-83 and HZ-88) were determined by the adsorption of two bases: pyridine and ammonia. The small molecules of ammonia penetrate the zeolitic channels much more easily than pyridine molecules. As the data presented in the Table show, the amounts of Brønsted sites determined with these two bases are comparable in both zeolites, thus giving evidence that pyridine may be used to determine the concentration of acid sites in ZSM-5 zeolites.

The present study deals with the acid properties of NaHZSM-5 zeolites of various exchange degrees prepared by two methods, namely by a "direct" exchange in HCl solution (HZ-series) and by the exchange in NH_4NO_3 solution and subsequent calcination *in situ* in the IR (NZ-series). It is therefore possible to discuss the acidic properties of NaHZSM-5 zeolites as a function of the exchange degree and also as a function of the mode of preparation.

The concentrations of Brønsted and Lewis acid sites were determined by quantitative IR studies of pyridine adsorption. Our experiments clearly show that two kinds of Brønsted site exist in NaHZSM-5 zeolites, 3609-cm^{-1} groups being strong acid sites and also other protonic sites of lower acidity. The concentrations of all these acid sites are presented in Figs. 4A and B. In both series of NaHZSM-5 zeolites (prepared by the exchange in NH_4NO_3 and HCl solutions) the total concentration of Brønsted acid sites increases linearly with the exchange degree. On the other hand, the concentrations of 3609-cm^{-1} OH groups and of weak acid sites do not increase linearly. The first protons introduced into the zeolite form weak acid sites and small amounts of 3609-cm^{-1} OH groups. The concentration of weak acid sites attains a constant value after the exchange of 30–40% of Na^+ ions and the introduction of the next protons results only in the formation of 3609-cm^{-1} OH groups. Such a sequence of site formation is observed in both series of NaHZSM-5 zeolites independently of the mode of preparation. The mode of introduction of protons into ZSM-5 zeolites does not influence either the sequence of sites formation or the proportion of strong and weak Brønsted acid sites.

It should be noted that the opinions expressed in earlier papers concerning the mode of hydrogen form preparation are not congruent. Rajadhyaksha and Anderson (*26*) reported differences in catalytic activity of zeolites exchanged by HCl and NH_4 salts: on the other hand, no such effects were observed by Auroux *et al.* (*10*). Our results show that no effect of the preparation mode on the number of sites of various kinds of exists. The influence of the mode of preparation on the acid site strength and catalytic activity of zeolites is under investigation.

According to the data presented in Fig. 5, the number of acid sites determined by IR spectroscopy is equal to the number of protons introduced into the zeolite during the ion exchange, augmented by the initial acidity of the NaZSM-5 parent form. This result is an argument in the discussion of the problem of influence of strong protonic acid sites on the properties of weaker sites. The authors (*6, 12*) postulated that strong protonic acid sites introduced into the zeolite in the course of ionic exchange increase the strength of weak sites preexisting in zeolite. Such a conclusion was drawn from the microcalorimetric and TPD studies in which the number of acid sites determined in the zeolite was about twice the number of protons introduced into the zeolite. In more recent studies the number of sites determined by microcalorimetrimetry and TPD (*10*, *13*) was found to be comparable with the number of Al atoms. These results, however, are not helpful in the discussion of "acidification" of weak acid sites by strong sites because neither the composition nor the initial acidity of the parent NaZSM-5 form were given, and the amount of protons introduced into the zeolite could not be calculated. As already stated, according to the results obtained in the present study the amount of acid sites determined spectroscopically is equal to the number or protons introduced into the zeolite augmented by the initial acidity of the sodium parent form, indicating that the introduction of protons does not result in any "acidification" of sites preexisting in the zeolite.

As already pointed out, the strong Brønsted acid sites are 3609-cm^{-1} OH groups. The nature of the weak Brønsted acid sites cannot be well defined. If we assume that these weak acid sites are OH groups, the IR band corresponding to them is expected to be very small or even not detectable, because the concentration of these sites is low (maximum of 0.3 per unit cell) and the extinction coefficient is also expected to be very small (the extinction coefficient decreases with the decrease of strength of OH groups). It is not excluded that weak Brønsted acid sites are OH groups vibrating at 3670 cm^{-1} (a very weak IR band at this frequency is observed in the spectrum).

It may be assumed that Lewis acid sites are formed in the dehydroxylation process. According to the results of IR studies obtained by the authors (*5*, *18*), the concentrations of Lewis and Brønsted acid sites in the zeolites activated at 770 K are comparable, thus indicating that dehydroxylation is advanced at this temperature. The calcination at higher temperatures resulted in a further dehydroxylation. On the other hand, in the case of NaHZSM-5 zeolites studied in the present research and activated at 723 K the concentration of Lewis acid sites was several times lower than that of Brønsted sites (Figs. 4A and B). The intensity of the OH band at 3609 cm^{-1} was constant to 873 K (the highest activation temperature used at the present work) (Fig. 1). All those observations prove that NaHZSM-5 zeolites studied at present are more resistant to dehydroxylation than those studied by the authors (*5*, *18*). It seems that this difference is due to difference in the Si/Al (47 and 19.5, respectively). The consequence of the high Si/Al ratio in our zeolites is the higher stability of the zeolite lattice and the lower density of acid sites which makes the dehydroxylation more difficult.

A small increase in the value of the integrated extinction coefficient of the 3609-cm^{-1} OH band denoted in the previous paragraph suggests an increase of the acid strength of these OH groups. Further studies are required in order to support this suggestion.

ACKNOWLEDGMENT

The authors thank Professor A. Bielański for helpful discussions.

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