

NMR Studies Concerning Bronsted Acidity of Zeolites

D. FREUDE, W. OEHME, H. SCHMIEDEL, AND B. STAUDTE

*Sektion Physik der Karl-Marx-Universität, Leipzig, NMR-Labor, DDR-701 Leipzig,
German Democratic Republic*

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NMR techniques have been used to study Bronsted acidity of decationated zeolites of A-, X-, and Y-types and of ion-exchanged zeolites. Number, thermal stability, and arrangement of OH groups have been determined. Furthermore, proton mobility and exchange times have been investigated. The probability of proton transfer from OH groups of different zeolites to a given adsorbed molecule represents a relative measure of Bronsted acidity.

INTRODUCTION

Bronsted acidity in zeolites results from the transfer of hydroxyl protons to adsorbed molecules. Different methods have been applied to study the nature of OH groups and their interaction with adsorbed molecules. Among these methods infrared spectroscopy especially deserves to be mentioned [e.g., see (1)]. The investigation of zeolites by means of proton magnetic resonance makes possible a direct determination of the number of OH groups. Moreover, by means of proton magnetic resonance measurements, some information about the arrangement of protons on zeolites [e.g., see (2)] can be derived. ^{13}C -NMR of adsorbed molecules is able to determine the ratio between the number of protonated to unprotonated molecules if the ^{13}C -spectra of the acidic and the basic forms of the molecules differ significantly. In addition to these data describing static behavior, the dynamic aspect of Bronsted acidity is of importance for a better understanding of catalytic processes as was pointed out by Tung (3). Characteristic parameters of a dynamic model are mean life times of protons and their activation energies, all of

which can be derived from NMR measurements (2). NMR studies of zeolitic OH groups have been made by several authors. For the number and arrangement of OH groups, we refer to (4) and (5); for proton motion, (6) and (7) should be mentioned.

In this paper, the number of OH groups is determined, by means of NMR, for various zeolites as a function of the method of pretreatment. From measurements of Hahn's echo we get information about the arrangement of OH groups in zeolites. Furthermore, mean lifetimes of protons in lattice diffusion or in proton exchange between OH groups and molecules are obtained from measurements of the temperature dependence of proton transverse relaxation times.

EXPERIMENTAL METHODS

Samples

Samples were prepared in general under deep-bed (DB) conditions (8). About 1 g of zeolite is heated in an open sample tube (12 mm in diameter) for 2 hr up to pretreatment temperature, and after an additional 2 hr it is evacuated carefully (10^{-2} -

$10^{-3} N/m^2$). In the following, the numbers before the type of zeolite denote the percentage of Na exchanged from the original Na-zeolite, and the numbers and letters after the type of zeolite denote temperature and method of pretreatment. 73 NaCeY 400 DB, for example, is a sample of Y-zeolite, in which 73% of the Na^+ was exchanged by Ce^{3+} , with activation being carried out at $400^\circ C$ under deep-bed conditions. 50 DeNaX 300 NB denotes zeolite X with 50% of the Na^+ exchanged with NH_4^+ ions. Here heating up to $300^\circ C$ was performed under vacuum (normal-bed). "De" refers to decationization caused by deamination. The so-called "normal-bed" condition corresponds to the pretreatment method of our samples used in earlier publications (5, 6). For some samples, we tried to attain shallow-bed (SB) conditions by very slow heating under high vacuum up to the activation temperature.

Si/Al ratios are 1.2 and 2.6 for zeolites X and Y, respectively. Adsorption onto the samples of water, perdeuterated pyridine, and perdeuterated benzene was done at room temperature and was proved by weighing.

Measurements

Stationary PMR spectra were measured using a wide-line spectrometer of bridge type (KRB 35/62, Akademiewerkstätten Berlin, GDR) at 21 MHz. Spin-echo measurements were carried out using a pulse spectrometer B-KR 322 (Bruker Karlsruhe, GFR) at 32 MHz and a home-made pulse spectrometer at 30 MHz. The low signal-to-noise ratio was improved by accumulation of spectra.

Measurements of intensity of hydroxyl protons (twofold integration of the detected derivative signal) and comparison with the proton intensity of a standard sample (an aqueous solution of manganese ions in a capillary) yielded the total number of OH

groups. Second moments (M_2), with an error of 10%, were obtained at liquid nitrogen temperature with the exception of Ce samples. For these, the second moment depends on frequency because of proton interaction with the paramagnetic Ce^{3+} ions. Therefore, Table 2 contains the frequency-independent term of the second moment for Ce samples at room temperature (9).

The time constant of the free induction decay T_2 of hydroxyl protons is only 20–40 μs because of the strong magnetic proton–aluminum interaction (4). The time constant for the decay of Hahn's echo T_2^* , which is determined by proton–proton magnetic dipolar interactions (10), is at least one order of magnitude greater than T_2 . Measurements of T_2^* have been carried out at $25^\circ C$.

In the following way we determined the number of protons for which the magnetic proton–proton interaction is much less than the magnetic proton–aluminum interaction. From a measurement of the amplitude $A(2\tau)$ of the echo at time 2τ (here τ is the time interval between the $\pi/2$ and π pulses) we obtain, by variation of τ , the relaxation time T_2^* and the coefficient "a" in the relation

$$A(2\tau) = a \exp\{-2\tau/T_2^*\},$$

which is valid for $\tau \gtrsim T_2$. The relative number of protons with dominating proton–aluminum interaction is, then, a/b , where b denotes the amplitude of the free induction signal at time $t = 0$. Recently, Schreiber and Vaughan (11) have applied a similar method to distinguish between SiOH and AlOH groups.

Correlation times of magnetic interaction energies can be obtained from the temperature dependence of transverse relaxation time T_2 or of line width. At the temperature of line narrowing onset (T_{2A} in Fig. 1), the correlation time τ_c for the interaction may be determined from the equation $\tau_c \gamma \sqrt{M_2} \approx 1$ [c.g., see (12)]. Here M_2 is the second

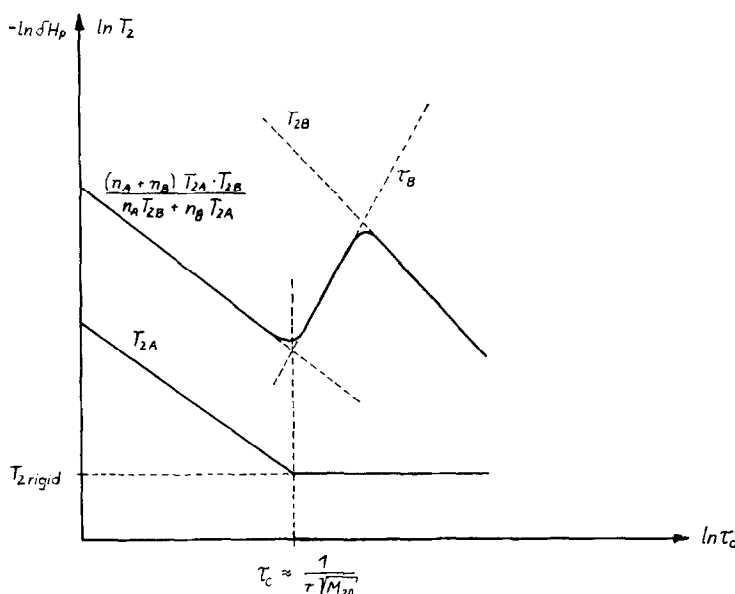


FIG. 1. Transverse relaxation time of ¹H versus correlation time in case of proton exchange between zeolitic OH groups (region A) and water molecules (region B).

moment of the NMR-line shape, which is determined by the nuclear magnetic interaction, and γ is the gyromagnetic ratio. The temperature dependence of line narrowing (or increase of transverse relaxation time T_2) is given by

$$1/T_2 = \gamma M_2 \tau_c, \text{ for which } \gamma \tau_c (M_2)^{\frac{1}{2}} \ll 1$$

and

$$\omega_0 \tau_c = \gamma H_0 \tau_c \gg 1.$$

Assuming that $\tau_c \propto \exp\{E/RT\}$ we can find an activation energy E . Instead of $1/T_2$ we have measured the "peak-to-peak" line width δH_p . For a line shape nearly Lorentzian, one has for protons

$$\delta H_p [\text{G}] \approx 43/T_2 [\mu\text{s}].$$

To interpret τ_c , we consider that all protons bound to the zeolite lattice are in group A. Protons of adsorbed molecules are considered to be in group B. The time constant τ_A is the mean lifetime of a proton in group A with respect to a transition to group B, and correspondingly, τ_B is the mean lifetime of a proton in group B. Finally, we

define the time τ_D as the mean lifetime of a hydroxyl proton at a lattice oxygen before jumping to another oxygen in the zeolite lattice. τ_c is equal to τ_D in the case of diffusion of hydroxyl protons over lattice sites if adsorbed molecules are absent or if adsorbed (perdeuterated) molecules of pyridine are present. Coverage with water at room temperature gives a narrow signal of mobile water molecules (relatively long T_{2B}) and a broad signal (relatively short T_{2A}) of hydroxyl protons. With a rise of temperature, proton exchange begins, and for $T_{2B} = \tau_B$, one observes a maximum in T_{2B} (cf. Fig. 1) and thus can determine τ_B . A detailed description of this method of determining τ_B can be found in reference (13).

If τ_A and τ_B are on the order of hours or longer, values of these time constants follow from a measurement of proton resonance line intensity using perdeuterated molecules in the following way. After adsorption of perdeuterated molecules, the zeolite is held for a given time at a certain

TABLE 1
Number of Hydroxyl Groups in Dehydrated Zeolites

Sample	M^a	Number of hydroxyl groups per cavity at activation temperature of		
		300°C	400°C	500°C
90 DeNaY DB	6.0	6.6	5.5	4.5
90 DeNaY NB	6.0	6.6	5.5	1.8
50 DeNaX DB	5.5	3.1	1.8	0.6
50 DeNaX NB	5.5	5.5	4.3	1.4
40 DeNaA DB	4.8	3.5	1.7	0.5
40 DeNaA NB	4.8	—	1.9	1.1
73 NaCeY DB	1.5	4.3	3.2	1.3
73 NaCeY NB	1.5	3.6	2.8	1.0
88 NaCaY DB	3.2	3.1	2.4	1.2
CaA NB	5.9	5.6	3.1	1.0

^a M denotes number of di- or tri-valent cations per cavity or (in case of decationated zeolites) deficiency of cations per cavity.

temperature, then the number of protons which have left group A for group B is determined by means of PMR. Measurements of proton lifetime τ_A were made at a coverage of about two molecules of perdeutero benzene to each cavity on decationated and CeY-zeolites. For this purpose, a set of samples was treated at 95 and 150°C for different times. The intensity of the narrow line which is caused by protons in the group of very mobile molecules was measured. This intensity can be described by a formula (see discussion) which yields τ_A .

EXPERIMENTAL RESULTS

The number of hydroxyl protons is listed in Table 1. In Table 1, M , in the case of decationated zeolites, is the maximum number of structural OH groups. For cation zeolites, M denotes the number of polyvalent ions, and, in this case, no simple relation between M and the number of OH groups can be given.

In addition, we have determined the total number of hydroxyl groups for the

following samples: 90 DeNaY 300 SB, 4.0 OH per cavity; 73 NaCeY 300 SB, 2.2 OH per cavity; 73 NaCeY 400 SB, 1.2 OH per cavity. The above numbers of OH groups refer to one cavity which corresponds to $\frac{1}{8}$ of the unit cell (14). Accuracy of the measurements carried out at room temperature is ± 0.3 OH per cavity. In agreement with the NMR data, thermogravimetric measurements show that dehydration is complete at 300°C (5).

In Table 2 the following values are given: a/b (fraction of isolated OH groups), second moment M_2 (mainly determined by proton-aluminium interaction), and T^*_2 (the relaxation time caused by proton-proton-interaction). It could be shown by additional experiments that the type of pretreatment (SB or DB) of the samples has no significant influence on the fraction of isolated OH groups. Figure 2 shows the temperature dependence of PMR-line width of samples 90 DeNaY 400 NB, 50 DeNaX 400 NB, 73 NaCeY 400 DB, and 88 NaCaY 400 DB, all samples having two molecules of perdeuterated pyridine per cavity. Sample 90 DeNaY 400 DB shows the same

TABLE 2

Transverse Relaxation Time T^*_2 (Measured by Means of Hahn's Echo), Fraction a/b of Protons with Predominant H-Al Interaction (Isolated OH Groups), and Second Moment M_2 .

Sample	$T^*_2[\mu s]$	a/b	$M_2[G^2]$
90 DeNaY 300 NB	240	1	0.96
90 DeNaY 500 NB	440	1	1.04
90 DeNaY 400 DB	270	1	0.96
50 DeNaX 300 NB	300	1	0.8
50 DeNaX 500 NB	500	$\frac{1}{2}$	—
40 DeNaA 300 NB	280	1	—
40 DeNaA 500 NB	1000	$\frac{1}{2}$	—
73 NaCeY 300 DB	250	$\frac{1}{2}$	1.0
73 NaCeY 400 DB	275	$\frac{1}{2}$	0.96
73 NaCeY 500 DB	630	$\frac{1}{2}$	—
88 NaCaY 300 DB	430	$\frac{1}{2}$	0.55
88 NaCaY 400 DB	700	$\frac{1}{2}$	0.50
88 NaCaY 500 DB	1000	$\frac{1}{2}$	—
CaA 300 NB	270	$\frac{1}{2}$	2.0
CaA 500 NB	>1000	$\frac{1}{8}$	—

temperature dependence of line width as the NB sample, but line shape analysis shows that motion of only a part of protons causes line narrowing. This may be explained by the fact that line width measurements strongly depend on narrow components of the line.

By splitting up the free induction decay into a long and a short phase, we obtain values for the number of OH groups which are responsible for line narrowing (see Table 3). Thus line narrowing is caused by motion of all OH groups in sample CeY (after 2 hr at 200°C), by half of the OH groups in samples DeX NB and Dey NB, and by about one-fifth of the OH groups in samples DeY DB and CaY DB. Values of the activation energies and correlation times at 0°C are given in Table 3. They are valid, however, only for the more mobile protons.

Figure 3 shows the temperature dependence of the proton transverse relaxation time T_2 for zeolites which have been covered at room temperature with H₂O after DB activation at 400°C. Surface coverage corresponds to 10 water molecules per cavity ($\theta = \frac{1}{3}$). For all three samples, in addition to the signal for which T_2 is plotted in Fig. 2, we observed a short phase signal caused by OH groups or water molecules in the cubooctahedron (sodalite cage), which has a decay time of about 30 μ s at room temperature.

We suggest that since the number of OH groups is not changed by hydration of the zeolite at room temperature, values of dehydrated samples (Table 1) can be used. This was proved by a method described in reference (5) and allows us to determine the number of OH groups in our partially hydrated zeolites at liquid nitrogen temperature. The following results were obtained: 90 DeNaY 400 DB, 5 ± 1 OH per cavity; 88 NaCaY 400 DB, 2.7 ± 0.5 OH per cavity; 73 NaCeY 400 DB, 3.5 ± 0.5 OH per cavity. Values of τ_A in the systems benzene-DeY and benzene-

CeY are given in Table 4. In Ce-zeolites a small portion of the OH groups (about 0.5 hydroxyls per cavity) is exchanged already at room temperature, contrary to decationated zeolites. The exchange time of this small part is too small to be measured by our method. The error in values τ_A is up to 50%, so that for both zeolites activation energy of the exchange is found to be about 15 ± 5 kcal/mole. In the case of 90 DeNaY DB zeolite covered with two molecules of pyridine per cavity, ¹³C spectra at 150°C yield equal amounts of pyridine molecules and pyridinium ions (15). However, evaluation of these amounts is complicated because of broadening of ¹³C-resonance lines caused by restricted motion of the adsorbed molecules especially at lower temperature.

DISCUSSION

Number and Arrangement of OH Groups

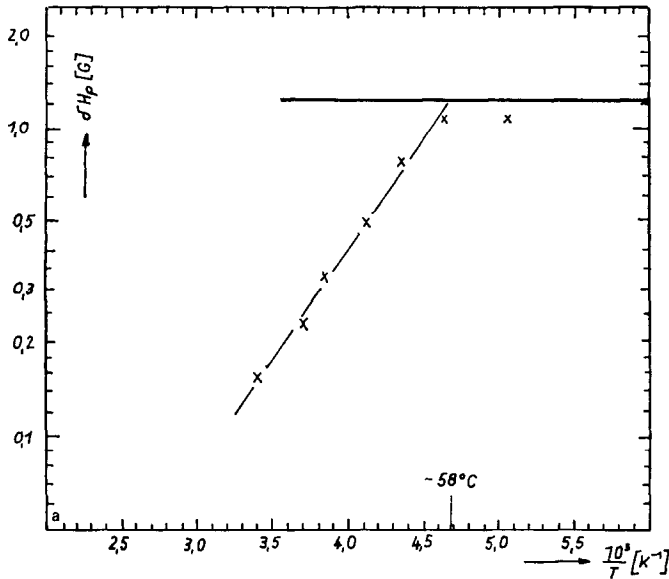
Different pretreatment of zeolites influences the number of OH groups and their thermal stability. Our deep-bed (DB) pretreatment is comparable to the one used by Kerr (8), but our shallow-bed (SB) pretreatment does not reach the shallow-bed conditions used in ir spectroscopy because of our relatively large sample volume (2 cm³). Nevertheless SB pretreatment of decationated and CeY-zeolites reduces the number of OH groups to one-half the OH content in the case of DB pretreatment.

As to NB and DB pretreatments, the stability of hydroxyl groups in decationated zeolites strongly depends on the type of zeolite. Sample 90 DeNaY between 300 and 400°C is insensitive to these kinds of pretreatment. Above 400°C one observes a higher stability of OH groups in the case of DB samples (see Table 1). DB pretreatment of decationated A- and X-zeolites, however, leads to lower hydroxyl contents, which at 300°C already are much less than the theoretical values assuming

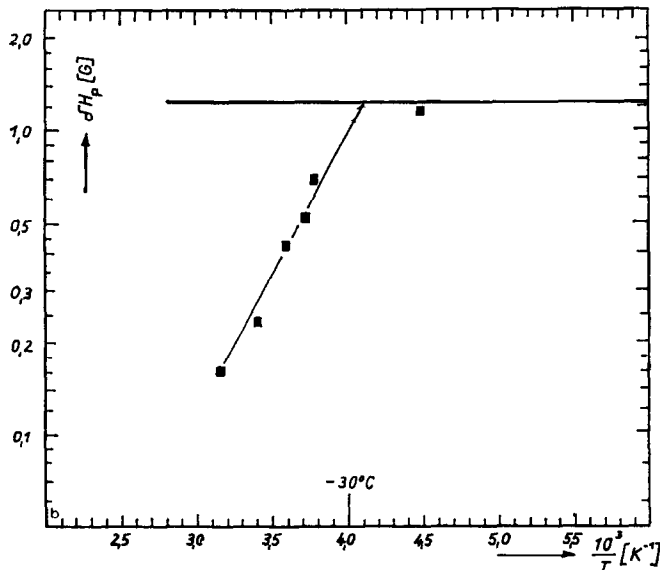
no dehydroxylation. Decrease of OH content in these samples cannot be caused by strong destruction of the zeolite lattice, because corresponding measurements did not show a decrease of adsorption capacity of water for samples 40 DeNaA 500 DB and 50 DeNaX 500 DB. Hydroxyl content of 73 NaCeY after DB pretreatment is

higher than that after NB pretreatment. This may be the result of hydrolysis of residual water molecules at higher temperatures which leads to an increase in the amount of thermally stable OH groups.

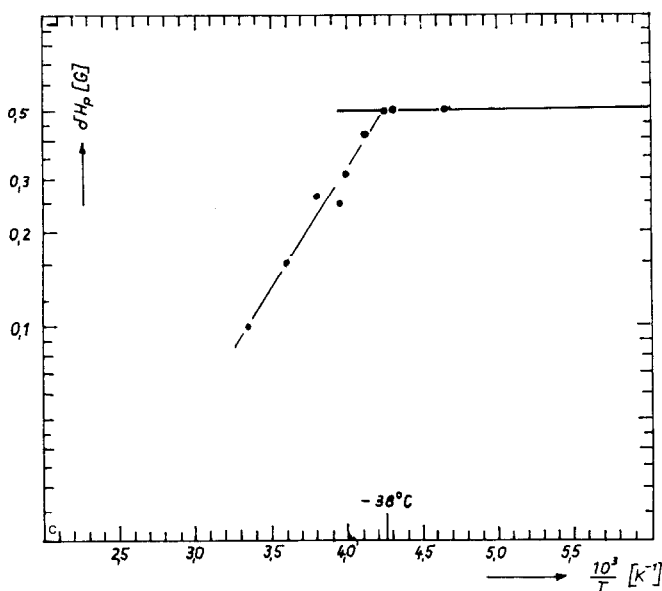
The NMR line shape of decationated Y-zeolites which is determined by the proton-aluminum magnetic dipolar inter-



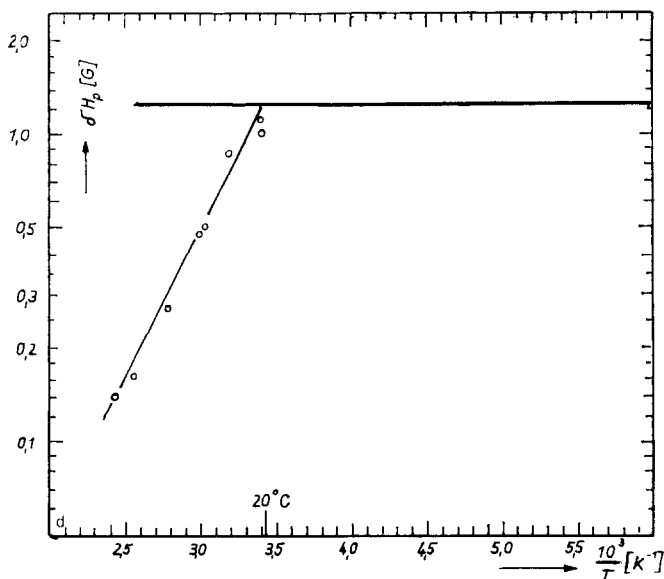
(a)



(b)



(c)



(d)

FIG. 2. Temperature dependence of δH_p for zeolites with a surface coverage of two molecules of pyridine per cavity. (a) 50 DeNaX 400 NB, (b) 90 DeNaY 400 NB, (c) 88 NaCaY 400 DB, and (d) 73 NaCeY 400 DB. The strong line is the value measured by temperature of liquid nitrogen.

action (4, 16), can be explained assuming statistical distribution of protons at sites determined by the oxygen framework of zeolite. For these sites nearest proton-

aluminium distance is 2.3 Å, and the minimum distance r_0 between two protons is about 2.5–3 Å (16). In this model of a statistical distribution of protons (isolated

TABLE 3

Correlation Time and Activation Energy of Proton Diffusion in Zeolites Covered with Two Pyridine Molecules per Cavity

Sample	$\tau_D[\mu\text{s}]$ at 0°C	$E_a[\text{kcal}/\text{mole}]$	n_A^a
90 DeNaY 400 NB	14	4.0	3.0 ± 0.5
90 DeNaY 400 DB	14	4.0	1.0 ± 0.5
50 DeNaX 400 NB	7	3.3	2.0 ± 0.5
73 NaCeY 400 DB	60	4.5	3.0 ± 0.5
88 NaCaY 400 DB	16	3.6	0.5 ± 0.2

^a n_A denotes number of OH groups per cavity which take part in diffusion.

OH groups), the probability of finding the nearest proton at a distance r from a given proton is proportional to r^2 and for $r < r_0$ this probability equals zero (17). T^*_2 can be calculated according to (10) and (17) as

$$T^*_2[\mu\text{s}] \approx 0.52/n [\text{\AA}^3].$$

Here n is the proton density determined from values in Table 1. The agreement between calculated and measured values of T^*_2 is a measure of validity of the above model. Our calculated values of T^*_2 do not differ by more than a factor of 1.6 from experimental values of T^*_2 . Therefore, it can be concluded that the model of statistical distribution is a good approximation for the arrangement of isolated OH groups.

Apart from isolated OH groups (their amount is given in Table 2, column a/b), cation zeolites contain OH groups with stronger proton-proton interactions. These so-called "neighboring" OH groups can arise both from $\text{Me}^{(n-2)+}(\text{OH})_2$ arrangements and from $\text{Me}^{(n-1)+}\text{OH}$ in the neighborhood of a lattice hydroxyl group. Our measurements are not able to distinguish between these two possibilities. The probability of having paired lattice OH groups (two OH groups at one Si atom) is small for the zeolite lattice. Only in decationated A-, and X-zeolites with a 500°C pretreatment temperature might paired OH groups arise (though we were able to exclude

strong destruction of lattice) because of the small fraction of isolated OH groups ($\frac{1}{4}$ and $\frac{1}{2}$, respectively) in these cases.

It is remarkable that the fraction of isolated OH groups does not increase with increasing pretreatment temperature in the case of cation zeolites. Hydroxyl group content of sample CaA 500 NB is five times less than that of sample CaA 300 NB (see Table 1). The fraction of isolated OH groups, however, for the 500°C sample is even smaller (see Table 2). This is true also for other zeolites exchanged with polyvalent ions. Therefore process of dehydroxylation cannot occur by creation of metal oxides because then structural OH groups should remain and could be detected as isolated groups.

OH groups in Ca zeolites of types A and Y show different behavior. For CaA mainly neighboring OH groups are present. The large value of the second moment $M_2 = 2.0 \text{ G}^2$ is understandable if there (5) is a distance of about 2.5 Å between neighboring protons. In sample 88 NaCaY 300 significantly more isolated OH groups

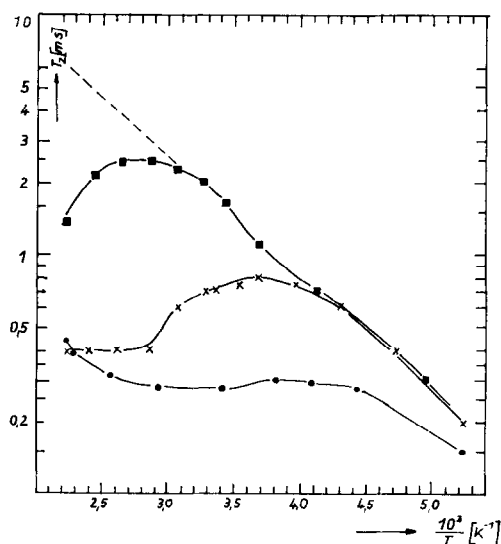


Fig. 3. Temperature dependence of T_2 for Y-zeolites with a water coverage of $\theta = \frac{1}{3}$; (O) 90 DeNaY 400 DB; (X) 73 NaCeY 400 DB; (□) 88 NaCaY 400 DB.

are present. The small value of 0.55 G^2 for the second moment gives an indication of the weakened proton–aluminium interaction. A detailed discussion of second moments, especially for decationated zeolites, is given in reference (5).

In the case of Ce-zeolites, the second moment caused by dipole–dipole interaction does not differ from that of decationated zeolites. Agreement of second moments, however, is no proof of equal proton arrangement in both zeolites, because only one half of the OH groups in Ce-zeolites are isolated. Some information about the number of CeOH^{2+} ions can be obtained from the frequency-dependent part of M_2 which itself is determined by proton interaction. Additional measurements of magnetic susceptibility (9) lead us to believe that 40% of the Ce ions are paramagnetic in the form of $\text{Ce}(\text{OH})^{2+}$.

By means of ir spectroscopy, Steinberg *et al.* (19) found five, six, and seven different types of OH groups in NaCaY DB, NaCeY DB, and DeNaY DB, respectively. The number of OH groups which is determined by means of D_2 exchange (19) is in good agreement with our values.

Proton Mobility

To describe the dynamic behavior of Bronsted acidity we have obtained, by NMR, the following four kinetic parameters: (a) mean lifetime of protons at an oxygen atom in dehydrated zeolites, (b) mean lifetime of protons at an oxygen atom in partially hydrated zeolites ($\theta \approx \frac{1}{3}$), (c) mean lifetime of protons at an oxygen atom in zeolites covered with two molecules pyridine per cavity, and (d) mean lifetime of protons on OH groups before transfer to benzene for zeolites containing two molecules of benzene per cavity.

(a) Mean lifetimes τ_D of protons at an oxygen atom correspond to correlation times and are obtained from the temperature dependence of proton relaxation on

TABLE 4
Exchange Times for Zeolites Covered with Two Molecules of C_6D_6 per Cavity

Sample	τ_A [hr]	
	at 95°C	at 150°C
90 DeNaY 400 DB	8	0.5
73 NaCeY 400 DB	300	16

dehydrated zeolites. At 400°C these measurements yield the following values of τ_D (in microseconds) [see also (6)]: 90 DeNaX 400 NB, ≈ 5 ; 90 DeNaY 400 NB, ≈ 20 ; 88 NaCaY 400 DB, ≈ 30 ; 73 NaCeY 400 DB, $\gtrsim 40$.

The decrease of mobility in the above sequence can be ascribed to an increase in bonding strength. This parameter, however, is of low importance as a measure, because “acidity” has no sense if adsorbed molecules are absent, and presently there is no model which is able to describe correctly the diffusion of protons over the oxygen framework of dehydrated zeolites. The existence of a very small amount of water or ammonia acting as “proton-transport vehicles” in the form of H_3O^+ or NH_4^+ ions cannot be excluded. Our previous arguments in reference (6) against the possible existence of these vehicles is not valid. In addition to our results in reference (6), we are now able to say that proton motion is not restricted to localized movement near the four oxygen atoms in the neighborhood of an aluminum atom. The longitudinal relaxation time of Al in zeolite was determined by Mestdagh *et al.* (20) and is much greater than the proton correlation time, so that we have a further indication of proton diffusion over the zeolite lattice.

(b) The mean lifetime τ_A of protons in OH groups can be obtained, in the case of hydrated zeolites, from the mean life time τ_B of the protons on water molecules by

TABLE 5
Mean Lifetime of Protons of Partially Hydrated
Zeolite at 0°C

Sample	$\tau_B(0^\circ\text{C})$ [ms]	$\tau_A(0^\circ\text{C})$ [ms]	$P(0^\circ\text{C})^a$
90 DeNaY 400 DB	0.3	80	67×10^3
73 NaCeY 400 DB	1.1	180	18×10^3
88 NaCaY 400 DB	5.5	600	4×10^3

^a P denotes mean number of proton transitions per cavity per second.

means of the following equation

$$\tau_A/\tau_B = n_A/n_B.$$

The number of water protons n_B is known from the water content. From Fig. 3, values of τ_B can be obtained. For samples 88 NaCaY 400 DB and 73 NaCeY 400 DB, values of τ_B equal 2.8 ms at 80°C and 1.1. ms at 0°C, respectively. For sample 90 DeNaY 400 DB, transverse relaxation time exhibits no distinct maximum so that the temperature value of -20°C for $\tau_B = 0.4$ ms has a relatively large error. The activation energy of τ_B cannot be obtained from the above measurements. However, using an approximate activation energy of 5 kcal/mole (which was measured by Pfeifer (21) for a hydrolyzed NaX-zeolite), experimental values of τ_B at 80 and -30°C yield theoretical values of τ_B at 0°C (see Table 5). Since it may be possible that not all OH groups take part in the exchange, the number of OH groups is only an upper limit for n_A .

With rising temperature, the maximum in T_2 in Fig. 1 is followed by a minimum in T_2 , where

$$T_{2\min} \approx 2\tau_B \approx 4[(n_A + n_B)/n_A] \cdot T_{2\text{rigid}}$$

is valid. $T_{2\text{rigid}}$ is the value of the transverse relaxation time for the OH signal in the case of a rigid lattice. With known values for $T_{2\text{rigid}}$ ($T_{2\text{rigid}} \approx 30 \mu\text{s}$) and $T_{2\min}$, one is able to estimate the number n_A . Thus in decationated and Ce-zeolites nearly all OH groups take part in the exchange.

The transverse relaxation T_2 for the Ca sample shows no minimum. Assuming that in this case all OH groups take part in the exchange, $\tau_A = \tau_B \cdot n_A/n_B$ can be calculated and is shown in Table 5. The quantity $n_A/c_A = n_B/\tau_B$ is a useful measure for activity of the proton exchange, because it is the mean number of proton transitions per cavity per second (see Table 5). A detailed discussion of proton exchange in NaX zeolites is given by Pfeifer (21, 22) and Murday *et al.* (23).

(c) A pyridine molecule and the proton of hydroxyl groups may form a pyridinium ion, which is, similar to water, a "transport vehicle." In contrast to water, however, deuterons on pyridine and hydroxyl protons do not exchange. This was proved experimentally for DeY- and CeY-zeolites, which were heated 24 hr at 400°C. The same result was obtained by Steinberg *et al.* (19) and Ward (24) by means of ir spectroscopy. Therefore, the quantities given in Table 3 correspond to the mean lifetime of a proton at an oxygen atom before transfer occurs to another oxygen atom through an intermediate ion.

An activation energy of about 4 kcal/mole (see Table 3) is necessary for proton transfer to pyridine and separation of the pyridinium ion from the donating oxygen atom.

According to Table 3, we have $\text{DeX} > \text{DeY} \approx \text{CaY} > \text{CeY}$ for zeolite activity with respect to a proton transfer to pyridine at 0°C. As was pointed out above, only some of the OH groups are interacting with pyridine. This is explained by the different accessibility of OH groups. It is known from ir investigations that only "HF-band" hydroxyls are influenced by pyridine adsorbed on DeY-zeolite (24). The part of OH groups which gives rise to the "HF band" is about 50% in the case of 90 DeNaY (25) and decreases significantly for deep-bed pretreatment (26).

(d) Group A represents the hydroxyl protons and group B the protons belonging

to adsorbed benzene molecules. n_A denotes the number of zeolitic OH and OD groups per cavity which take part in the exchange, and n_B is the corresponding number for group B. The mean lifetime of protons and deuterons within group A is τ_A , and τ_B denotes the same quantity for group B. At equilibrium we can show that there is no isotope effect, whereas in the system D_2O -DeY an isotope effect is observed (18). The number $N_A(t)$ of protons per cavity in region A at time t is obtained from

$$[dN_B(t)/dt] = [N_A(t)/\tau_A] - [N_B(t)/\tau_B].$$

Using perdeuterated molecules, we have as initial values $N_A(0) = n_A$, $N_B(0) = 0$, and $N_A(t) + N_B(t) = n_A$.

Solution of the equation above yields

$$N_B(t) = \{n_A/[1 + (n_A/n_B)]\} \\ \times \{1 - \exp[-(t/\tau_A)(1 + (n_A/n_B))]\}.$$

By means of this solution one can determine τ_A , if n_A and n_B are known and $N_B(t)$ is measured at different times t . In Table 4 values of τ_A in the case of 90 DeNaY 400 DB are valid for all OH groups. Certainly direct exchange occurs by proton transfer only from accessible hydroxyl groups to benzene molecules. However, the exchange time is so long that during this time exchanged deuterons will diffuse over the whole zeolite lattice.

For the major fraction of OH groups in Ce-zeolite, the exchange time is more than one order of magnitude longer than in the case of decationated zeolite, so that the activity in DeY is higher than in CeY. For about $\frac{1}{2}$ of the OH groups per cavity in Ce-zeolite, activity is higher than in DeY-zeolite. Mean lifetimes, which are determined according to methods (a) through (d), give some idea about the velocity of proton diffusion or proton transfer in different systems. Inverse life times in cases (b), (c), and (d) represent velocity constants of corresponding chemical reactions; e.g., of proton exchange in cases (b) and (d). For a given adsorbed molecule,

the inverse lifetime is proportional to the activity a^+_{H} of "free" protons. Thus the inverse lifetime at a given adsorbed molecule represents a relative measure of acid strength, which can be defined and measured absolutely for zeolites using Hammett indicators (27, 28). Our measurements yield the following sequence of acid strength: 50 DeNaX 400 > 90 DeNaY 400 > 88 NaCaY 400 > 73 NaCeY 400, with exception of (b) where the acid strength of the Ce sample is stronger than that of the Ca-zeolite.

This suggests that acidity equals the concentration of acidic OH groups and that an absolute measure of acidity is given by the number of OH groups in Table 1, where one has only to take into account that in some reactions only part of the OH groups may be involved. Multiplication of the number of acidic OH groups per cavity by $1/\tau_A$ gives the probability of proton transfer per second per cavity, which represents an unambiguous measure of acidity for different types of zeolites and a given molecule.

CONCLUSIONS

A

Compared with continuous heating during 30 hr under vacuum up to final temperature, deep-bed calcination yields an enhanced thermal stability of OH groups above 400°C for DeY-zeolites and an enhanced number of OH groups in CeY-zeolites. In the case of DeX- and DeA-zeolites, however, deep-bed calcination decreases the number of hydroxyl groups.

B

Hydroxyl groups in decationated Y-zeolites (400°C calcination temperature) are distributed statistically at sites which are given by positions of the lattice oxygen atoms. However, about one-half of the OH groups consists of neighboring groups in Y-zeolites exchanged with di- and trivalent ions. This part does not decrease with increasing pretreatment temperature, and

therefore dehydroxylation (up to 600°C) does not proceed predominantly according to the reactions $2 (\text{MeOH})^+ \rightarrow \text{H}_2\text{O} + \text{MeO} + \text{Me}^{2+}$ or $2 (\text{MeOH})^+ \rightarrow \text{H}_2\text{O} + \text{Me}^+ + \text{O}-\text{Me}^+$.

C

Values for the mean lifetime of protons at an oxygen atom at 400°C for dehydrated zeolites are about 5, 20, 30, and $\gtrsim 40 \mu\text{s}$ for DeX-, DeY-, CaY-, and CeY-zeolites, respectively.

D

Values for the lifetime of protons within the region of lattice oxygens before going to water molecules at 0°C in partially hydrated zeolites ($\theta = \frac{1}{3}$) are 80, 180, and 600 μs for DeY-, CeY-, and CaY-zeolites, respectively.

E

Values for the mean lifetime of a proton at a lattice oxygen (before going over to a pyridine molecule and thus forming a pyridinium ion) for zeolites covered with two molecules of pyridine per cavity, are (at 0°C) 7, 14, 16, and 60 μs in the case of DeX-, DeY-, CaY-, and CeY-zeolites, respectively.

F

Values for the mean lifetime of a proton within the region of OH groups (before going over to a benzene molecule) in zeolites covered with two molecules of benzene per cavity, are (at 150°C) 0.5 and 16 hr for DeY- and CeY-zeolites respectively.

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