JOURNAL OF CATALYSIS 32, 137–143 (1974)

NMR Investigation of Proton Mobility in Zeolites

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Received July 27, 1973

Using instationary pulse techniques in addition to stationary wide line measurements conclusion could be drawn concerning mobility of protons corresponding to the OH groups in decationated zeolites of A-, X- and Y-types and in ion exchanged zeolites.

At 200°C proton jump between lattice oxygen atoms with frequency $(2\text{–}10) \times 10^4\ s^{-1}$ and activation energy 5–10 kcal/mole for dehydrated decationated zeolites. Adsorption of pyridine increases proton jump frequency.

INTRODUCTION

Proton mobility of structural hydroxyl groups is necessary for Brønsted acidity of OH groups and for dehydroxylation of zeolites. Infrared spectroscopy which is commonly used for an investigation of OH groups [see e.g. (*1*, *2*)] is not able to yield definitive information about such motions (*3*, *3a*).

Firstly we obtained by means of NMR proton jump frequencies of about $10^4\ s^{-1}$ at 100°C from measurements of temperature dependence of NMR line width (*4*). These values have been verified by measurements of the special NMR-relaxation times T_{2eff} (*5*) and T_2^* (*6*). Mestdagh, Stone and Fripiat (*7*) drew conclusions about proton mobility in decationated Y-zeolite by investigation of the temperature dependence of the second moment M_2 and of the transverse (T_2) and longitudinal (T_1) relaxation times. Their method of calculating proton jump frequencies is dubious because it is based on some extrapolation of experimental data and on the assumption of the same relaxation mechanism for T_1 and T_2.

In the present work proton jump frequencies and activation energies will be obtained from measurements of temperature dependence of proton line width and of T_{2eff} in decationated A-, X- and Y-zeolites. Furthermore some results are given for zeolites exchanged with Me^{2+} and Me^{3+} ions. First conclusions have been drawn about the mobility of protons interacting with adsorbed molecules of pyridine in 90-DeNaY–zeolites. A detailed discussion of number and arrangement of OH groups in zeolites used in this work may be found in Ref. (*8*).

EXPERIMENTAL METHODS

Samples

Samples have been prepared from commercial Na-zeolites by ion exchange at "Zentralinstitut für Physikalische Chemie der Akademie der Wissenschaften der DDR."

After 30 hr heating step by step up to 300°C *in vacuo* (about 10^{-1} Torr) of 1 g zeolite for each NMR sample has been evacuated (10^{-4}–10^{-5} Torr) for 20 hr at chosen pretreatment temperature.

In the following the degree of decationization and the pretreatment temperature of our samples will be described by the numbers before and after symbol of decationated zeolite, respectively. Therefore 90 DeNaY 300 denotes a Na-Y-zeolite where 90% of Na^+ ions are exchanged by NH_4^+ ions and which has been pretreated at 300°C.

Si/Al ratio is 1.2 and 2.6 for X- and Y-zeolites, respectively. It could be shown by X-ray measurements, that no deficiency of crystallinity occurred by pretreatment of decationated A-zeolites. Y-zeolites contained 700 ppm of paramagnetic Fe^{3+} ions.

Adsorption of perdeuterated pyridine (degree of perdeuteration 99%) has been accomplished after outgassing of pyridine. In the following we denote samples without adsorbed molecules as "dehydrated samples."

Measurements

Stationary NMR spectra were measured using a wide-line spectrometer of the bridge type (KRB 35/62, Akademiewerkstätten Berlin) at 21 MHz.

The signal-to-noise ratio could be improved by accumulation of several spectra with a spectrum accumulator IRA 1 (JEOL), to such a degree that the error of line width became less than 10% [cf. (*9*)]. Modulation, rf-field and time constant of phase sensitive detection have been chosen so that no additional error occurred.

For the temperature at which line narrowing begins we obtain a correlation time τ_c using the formula $\tau_c(M_2)^{1/2} \approx 1$ [cf. (*10*) or (*11*)]. Here M_2 is the second moment or that part of the second moment which is caused by the interaction of interest (e.g., H–Al or H–H interaction) and τ_c is the correlation time of interaction. Temperature dependence of line width is described by $1/T_2 = M_2\tau_c$ $[\tau_c(M_2)^{1/2} \ll 1, \omega_0\tau_c \gg 1]$ and $\tau_c \propto \exp(E/RT)$ with activation energy E.

Instead of $1/T_2$ we measured the so called "double line width" δH_d because there is less experimental error in determination of line width of derivative signal (*9*). For line shape near Lorentzian we have T_2 (μs) $\approx 103/\delta H_d$(G).

$T_{2\mathrm{eff}}$ was measured using a high-resolution spin-echo spectrometer for solids (*12*) at 60 MHz and a spectrum accumulator DIDAC 800 (INTERTECHNIQUE). From temperature dependence of $T_{2\mathrm{eff}}$ {decay time of "solid echo" envelope in the pulse sequence $(\pi/2)_y - [\tau - (\pi/2)_x - \tau]_n$} one is able to obtain correlation times (correlation time at $T_{2\mathrm{eff}}$ – minimum corresponds to pulse spacing time τ) and activation energies (slope of $T_{2\mathrm{eff}}$) (*5*).

Experimental Results

No measurements were carried out at temperatures above pretreatment temperature of the samples because of possible influence of dehydroxylation water molecules on proton mobility. We restricted our measurements to temperatures from 20 to 300°C or 400°C, because the line shape of dehydrated samples did not change from −196°C to room temperature. Line width has been investigated from −196°C to +300°C for samples with adsorbed molecules.

Figures 1 and 2 show the temperature dependence of δH_d and $T_{2\mathrm{eff}}$ for dehydrated 50 DeNaX–zeolites. Table 1 contains correlation times and activation energies obtained from temperature dependence of line widths and of $T_{2\mathrm{eff}}$ values. The correlation times determined from the minimum of $T_{2\mathrm{eff}}$ differ by a factor of two to four from those obtained from the onset of line width narrowing. This difference may be explained by the fact, that determination from line width narrowing data has an uncertainty factor of about two. Moreover a $T_{2\mathrm{eff}}$-pulse sequence influences H–Al and H–H interactions in some different way so that small differences may occur be-

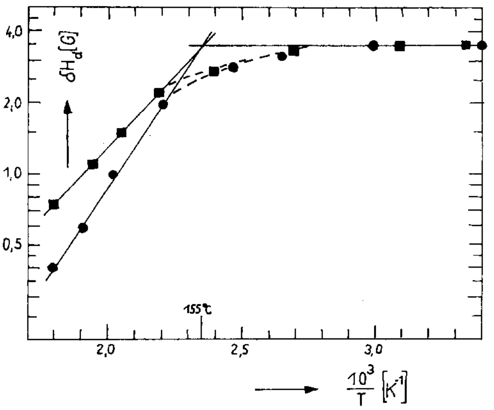

FIG. 1. Temperature dependence of δH_d for X-zeolites: (●) 50 DeNaX 300; (■) 50 DeNaX 400.

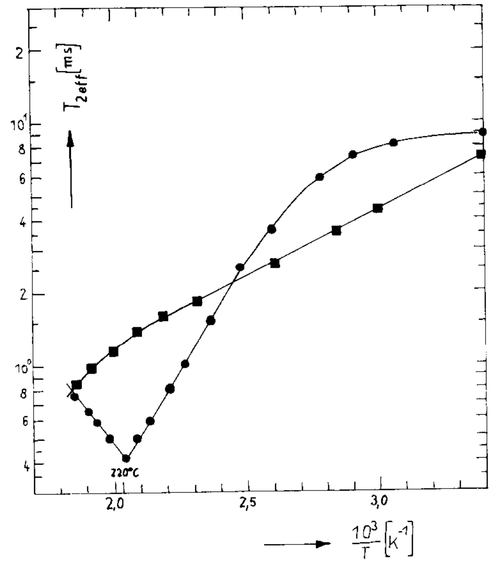

FIG. 2. Temperature dependence of T_{2eff} for X-zeolites: (●) 50 DeNaX 300; (■) 50 DeNaX 400.

tween correlation times obtained by T_{2eff} and δH_d methods. Activation energies determined from T_{2eff} and from δH_d are nearly the same with the only exception of 90 DeNaY 400 sample, where for T_{2eff} a process of higher activation energy must be taken into account, which influences δH_d only above maximum measurement temperature. No significant narrowing of δH_d has been observed for CaA 300 and NaCeY 300 samples up to 300°C. Below 300°C T_{2eff} also did not change with temperature for CaA 300, SrA 300, CaA 400 and NaMgA 300. Only weak temperature dependence of T_{2eff} up to 300°C was observable for NaCeY 300 and NaLaY 300. Thus here we have a relatively long correlation time at 300°C being longer than 10^{-4} s.

NMR line widths of OH groups are shown in Fig. 3 for 90 DeNaY 300 and 90 DeNaY 400 zeolites without and with a surface coverage of two molecules of pyridine per cavity.

For a coverage of only half a molecule per cavity there is no change of line width observable relative to the dehydrated samples. Though differing for 300 and 400°C pretreatment temperature for dehydrated samples the temperature dependence of line width of OH groups does not differ (within the error of experiment) for samples with two pyridine molecules per cavity. Activation energy and correlation time are 4 kcal/mole and 3×10^{-5} s (at −30°C), respectively. By extrapolation of temperature dependence up to 200°C one obtains for τ_c values of 3×10^{-5} and 5×10^{-7} s

TABLE 1

CORRELATION TIME τ_c AND ACTIVATION ENERGY OBTAINED FROM THE TEMPERATURE DEPENDENCE OF δH_d AND T_{2eff}[a]

	δH_d				T_{2eff}			
		τ_c (μs)				τ_c (μs)		
Sample	T_0 (°C)	For 200°C	For 300°C	Activation energy (kcal/mole)	T_M (°C)	For 200°C	For 300°C	Activation energy (kcal/mole)
30 DeNaA 300	90	7	3	5	160	30	6	8
40 DeNaA 300	170	19	4	10	210	70	15	8
40 DeNaA 350	210	41	7	10	—	—	—	—
50 DeNaX 300	150	15	4	8	215	70	20	8
50 DeNaX 400	150	19	7	5.5	>300	—	—	2–6
90 DeNaY 300	170	24	5	8	>300	—	—	10
90 DeNaY 400	170	30	21	2	>300	—	—	11

[a] T_0 is the temperature of the onset of the line width, T_M is the temperature of the T_{2eff}-minimum. The correlation time at the temperature T_0 is $M_2^{-1/2}$, for all samples about 40 μs [values for M_2 of these samples see Ref. (8)]. τ_c at T_M is 60 μs.

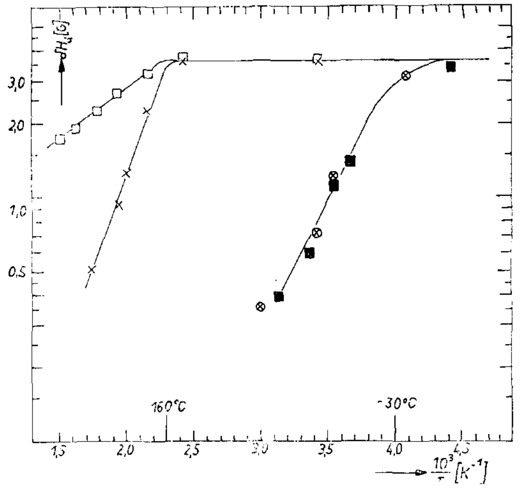

FIG. 3. Temperature dependence of δH_d for Y-zeolites without and with a surface coverage of two molecules of pyridine per cavity: (×) 90 DeNaY 300; (□) 90 DeNaY 400; (⊗) 90 DeNaY 300–2 pyridine/cavity; (■) 90 DeNaY 400–2 pyridine/cavity.

for samples without and with adsorbed molecules, respectively, i.e., the jump frequency of OH protons at 200°C has been increased by a factor of about 60 because of adsorption of two pyridine molecules per cavity.

The adsorption of two molecules of toluene per cavity on 75 DeNaY 300 sample increased the jump frequency of hydroxyl protons only by a factor of about two relative to the sample without adsorbate.

DISCUSSION

Mestdagh, Stone and Fripiat (*7*) measured the temperature dependence of longitudinal relaxation time of OH protons in decationated Y-zeolite. But as is well known no direct determination of correlation times is possible if one does not observe a minimum of T_1.

We measured the frequency dependence of T_1 at room temperature for a 75 DeNaY 300 sample using a BRUKER B-KR 322 s spin-echo spectrometer and obtained 4.65, 2.95 and 1.5 s at resonance frequencies ν_0 of 60, 32 and 16 MHz, respectively. Taking into account only proton–aluminum interaction the calculated T_1 values are considerably greater than the experimental data. The interaction of protons with paramagnetic impurities certainly influences T_1, because our T_1 values differ from those measured by Mestdagh, Stone and Fripiat (*7*) by a factor of two corresponding to half the amount of paramagnetic impurities in our samples. A correct determination of the effects causing T_1 is very difficult.

Line narrowing can be caused only by averaging to zero interactions which determine line width, in our case the H–Al and H–H interactions. In the case of proton–aluminum interaction both the motion of protons (characterized by a correlation time τ_c^{IS}, mobility of protons is much greater than that of aluminum) and the longitudinal relaxation of aluminum (characterized by the relaxation time T_1^{S}) determine the effective correlation time τ_c

$$\frac{1}{\tau_c} = \frac{1}{T_1^{\mathrm{S}}} + \frac{1}{\tau_c^{\mathrm{IS}}}$$

and may cause proton line narrowing.

We were not able to measure T_1^{S} for ^{27}Al nuclei in the vicinity of an OH proton, because the ^{27}Al line is not observable on account of a strong line broadening in the case of 90 DeNaY. On the other hand ^{27}Al line widths up to 40 G have been observed for various cationated zeolites. Therefore we conclude that the tetrahedrical symmetry of the electric field gradient at the Al sites will be very much disturbed by protons at neighboring oxygen atoms.

However it is very important to distinguish within τ_c ^{27}Al relaxation effects from proton mobility. Referring to different τ_c for different pretreatment temperatures of zeolite (e.g., 300°C and 400°C, cf. Table 1) we drew the conclusion (*14*) that the motion of protons dominates τ_c and causes line narrowing because one would not expect a difference in T_1^{S} for Al nuclei in the direct vicinity of protons (only such Al atoms are of interest).

Whereas proton–aluminum interaction may be averaged both by proton motion and by T_1^{S} proton–proton interaction can be averaged only by a motion of protons.

We obtained the rigid lattice line width of pure proton–proton interaction in zeolites by spin-echo experiments at room temperature (*6, 8*) ($T_2{}^*$ does not change from -196 to 20°C). For the 90 DeNaY 300 sample ($\delta H_d = 3.6$ G at room temperature) δH_d is narrowed at 300°C to 500 mG ($T_2 = 206$ μs), whereas for proton–proton interaction (at room temperature) we obtained $T_2{}^{\mathrm{II}} = 160$ μs (*8*). Therefore at 300°C proton–proton interaction is already partially averaged. The same fact is observed for 50 DeNaX 300 and 40 DeNaA 300 samples. Thus it is proved that for these samples line narrowing is caused by proton motion. Though we were not able to show this for all of our samples we shall assume in the following that line narrowing is always caused by motion of protons.

We define for further discussion a jump of a proton as motion between two stable positions near oxygen atoms. If we assume that oxygen is sp^3 hybridized and that the proton may jump between two orbitals the line width could be reduced only by 20% for sufficiently high jump frequency. Proton aluminum interaction can be averaged to zero by statistical jumps of protons between four oxygen atoms neighboring one aluminum atom. In this case we have $\tau_c{}^{\mathrm{IS}} \approx \tau_v{}^{\mathrm{Al}}$, where $\tau_v{}^{\mathrm{Al}}$ is the mean life time of a proton at an oxygen atom. This process of proton motion is able to reduce proton–proton interaction only (for samples with high OH coverage) by a factor of about ¼.

A complete averaging of proton–proton interaction occurs only in the case of statistical proton jumping between arbitrary oxygen atoms (most probably between neighbored oxygen atoms). By this motional process of course proton aluminum interaction also is averaged to zero. Here we have $\tau_c{}^{\mathrm{IS}} \approx \tau_v{}^{\mathrm{Si}}$ where $\tau_v{}^{\mathrm{Si}}$ is the mean life time of a proton at the four oxygen atom neighboring one aluminum atom. $\tau_c{}^{\mathrm{II}}$ is at least one order of magnitude larger than $\tau_v{}^{\mathrm{Si}}$ because of the greater number of jumps necessary for averaging (to zero) proton–proton interaction.

As the observed line narrowing factors are greater than two one is not able to explain this motional narrowing by localized jumps between the orbitals of one sp^3 hybridized oxygen atom and we have to conclude that the correlation times obtained from line width narrowing correspond to inverse jump frequencies of protons between different oxygen atoms. Unfortunately by means of our NMR measurements we are not able to distinguish (localized) jumps between the four Al neighbored oxygen atoms from (delocalized) jumps between arbitrary oxygen atoms. The energy barrier for (delocalized) jumps over Si atoms is possibly some higher than the energy barrier for (localized) jumps near one Al atom because of electrostatic interaction between proton and aluminum.

Molecules of pyridine often have been used for investigating the "acidic" character of OH groups by means of ir spectroscopy [see Ref. (*1*)]. There have been observed frequency shifts of the OH-stretching mode and spectra typical for pyridinium ions and for pyridine molecules chemisorbed at Lewis centers (*1*). Pyridine molecules chemisorbed at Lewis centers will be relatively immobile. Therefore it seems reasonable that low pyridine coverage does not influence the mobility of hydroxyl protons. If, however, all high energy sites are filled up the formation of pyridinium ions becomes more probable. Pyridinium ions cause proton motion because during pyridinium ion composition and decomposition a hydroxyl proton must be first attached by the pyridine molecule and then given back to another oxygen atom.

A similar motional process (by help of H_2O or NH_3) can be excluded for dehydrated samples because of the high activation energy of about 30 kcal/mole for H_2O or NH_3 molecules remaining in the zeolite after the above described pretreatment of samples. We have obtained activation energies of 5–10 kcal/mole for proton motion.

It is reasonable to compare the activation energies of samples with adsorbed pyridine molecules (about 4 kcal/mole) with the energy necessary for proton transfer from lattice oxygen to pyridine and separation of the pyridinium ion from lattice oxygen. Deininger and Reimann (*17*) (in this work mobility of adsorbed molecules and not of OH protons is examined) obtained an activation energy of 3 kcal/mole for the separation of pyridinium ions.

Thus interaction between OH groups and adsorbed molecules decreases the activation energy necessary for proton motion and increases proton jump frequency. This effect has been earlier observed by Pfeifer and Staudte (*18*) for hydroxyl groups on silica gel. A further affirmation of this statement arises from the fact that adsorbed pyridine and toluene cause a high and low increase of jump frequency, respectively. Interaction of OH groups with toluene is small compared to that with pyridine [see, e.g. (*1*)].

Brønsted acidity of zeolite OH groups is connected with proton mobility. Investigating proton mobility in zeolites without adsorbed molecules only indirect conclusions can be made about acidity of zeolites because acidity depends on the presence of a base. Reduced proton mobility in zeolites exchanged with Me^{2+} or Me^{3+} ions is a hint to a stronger bond of protons in these zeolites.

It is remarkable that jump frequencies of protons in decationated zeolites at 200°C are of the same order of magnitude as are jump frequencies of ions measured by means of NMR in Li-zeolites (*19*) and by means of NMR and dielectric relaxation in Tl-zeolites (*20*). This supports Tung's model (*21*) of dynamic Brønsted acidity where ion motion causes a time fluctuating Brønsted acidity. We have to remark, however, that our experiments and those carried out by Tung for establishing his model dealt with dehydrated zeolite (without adsorbed molecules) for which acidity is not defined.

In the case of decationated Y-zeolites with adsorbed molecules proton jump frequencies are directly connected with acidity. Assuming that acidity corresponds to the number of free protons and supposing that the mean life time of protons at lattice oxygen atoms is much greater than the time the proton is "free," we find that acidity is proportional to the product of (acidic) OH groups and proton jump frequency. The latter is essentially influenced by interaction between molecules and OH groups. The interpretation of acidity above mentioned seems to be more reasonable than setting acidity simply to be the number of (acidic) OH groups.

Unfortunately no direct conclusion can be drawn about proton mobility in the presence of adsorbed molecules at a temperature of 400°C from experiments carried out until now because of the uncertainty in extrapolation of experimental data from the room temperature region to higher temperatures. The region of temperature near 400°C is of special interest because of catalytic reactions occurring at those temperatures.

For dehydroxylation of zeolite both proton mobility and separation of whole OH groups from the zeolite lattice are necessary. Oehme (*22*) has measured dehydroxylation activation energies of decationated A-, X- and Y-zeolites and of their Me^{2+} exchanged forms in the following way:

Samples were activated for 20 hr in high vacuum at 300 or 400°C. Afterwards pressure was measured in dependence of temperature (300 to 400°C, or 400 to 500°C). Assuming $p \propto \exp(E/RT)$ for the pressure of dehydroxylation water molecules, activation energies E of 30–60 kcal/mole were obtained.

Rouxhet *et al.* (*23*) observed an activation energy of 47 kcal/mole for dehydroxylation in muscovite. Cattanach, Wu and Venuto (*24*) obtained an activation energy of 70 kcal/mole for dehydroxylation of decationated Y-zeolite by means of differential-thermogravimetric measurements.

These activation energies of about 50 kcal/mole certainly correspond to energy necessary for separation of OH groups. The activation energy of proton motion (separation of protons) of 5–10 kcal/mole and the activation energy of intracrystalline diffusion of water molecules (which is certainly of interest for dehydroxylation and which has been measured by Kärger (*25*) for NaX-zeolite to be 4.5 kcal/mole) are much smaller than the energy necessary for separation of OH groups.

CONCLUSIONS

a. Activation energy of proton jumps between lattice oxygen atoms is in the range of 5–10 kcal/mole for decationated A-, X- and Y-zeolites whereas activation energies of dehydroxylation amount to about 60 kcal/mole.

b. Proton jump frequencies (inverse mean life times at lattice oxygen atoms) number about 5×10^4 s^{-1} for dehydrated decationated zeolites at 200°C whereas this value of jump frequency is attained only at temperatures above 300°C for dehydrated zeolites exchanged with Me^{2+} and Me^{3+} ions.

c. At 300°C for decationated Y-zeolite with a pretreatment temperature of 300°C proton jump frequency is about four times higher than that for the same zeolite pretreated at 400°C.

d. Adsorption of two pyridine molecules per cavity on 90 DeNaY–zeolite increases hydroxyl proton jump frequency which amounts to 3×10^4 s^{-1} at −30°C. At 200°C this proton jump frequency is about 60 times higher than is the case without adsorbed pyridine. Adsorption of toluene only slightly increases (hydroxyl) proton jump frequency (by factor of about two).

ACKNOWLEDGMENTS

We are indebted to Professor Dr. H. Pfeifer for helpful discussions. We also thank Professor Dr. W. Schirmer, Dr. H. Stach, Dr. U. Lohse of the ZIPC of the Academy of Sciences, Berlin, for valuable advice and Mrs. G. Kratzsch and Mrs. D. Prager for carrying out some of the measurements.

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