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NMR investigation of proton mobility in zeolites

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Abstract

H-Y and H-ZSM-5 zeolites were investigated by ^{1}H MAS NMR spectroscopy over a wide range of temperatures (160–773 K). Signal broadening by up to a factor of 5 and signal narrowing by up to a factor of 40 could be assigned to different hydrogen-exchange reactions in the zeolites. We found that hydrogen forms of a zeolite containing ammonium ions represent ammonium-conducting materials, but in zeolites that were activated at temperatures above 673 K, the hopping of the hydrogen atoms between different aluminum sites (≡SiOHAl≡) is independent of proton vehicles.

Keywords: Brønsted site; Proton mobility; Zeolites; Ammonium; ^{1}H MAS NMR spectroscopy

1. Introduction

Bridging hydroxyl groups are capable of donating protons to molecules in the cages of zeolites. Proton transfer from the Brønsted acid site to molecules is an important elementary step in heterogeneously catalyzed reactions. In addition, the mobility of these protons and the dependence on a vehicle mechanism also are important to the discussion of the charge transport in solid electrolytes.

^{1}H NMR studies of the acid protons in dehydrated zeolites have provided some insight into proton mobility [1–3]. Sarv et al. [2], through temperature-dependent measurements of the second moment of the ^{1}H NMR, obtained line shape activation energies of 45, 54, and 61 kJ mol^{-1} for zeolites H-ZSM-5, H-mordenite and H-Y, respectively, and explained the corresponding mobility with proton jumps in the first coordination sphere of the aluminum atom in the Brønsted site. Baba and Ono [3], from the temperature dependence of the ^{1}H MAS NMR central lines, obtained activation energies of 17–20 kJ mol^{-1} for the thermal motion of the protons in the zeolite H-ZSM-5. Ernst et al. [4], monitoring the ^{1}H NMR line width of bridging OH groups in zeolite H-ZSM-5, observed a narrowing by a factor of 55 in the temperature range of 160–790 K, obtained an activation energy of 78 kJ mol^{-1}, and explained the proton mobility by one-site and multiple-site hopping. The role of a proton vehicle transport has been controversial for many years (e.g., [5–8]).

H-Y and H-ZSM-5 are the most important zeolite types for heterogeneously catalyzed reactions. After activation of the zeolites by either continuous carrier gas flow or vacuum treatment at higher temperatures, they still contain a small concentration of water molecules (or, in the ammonium-exchanged zeolites, ammonium ions). It remains unclear whether a proton vehicle mechanism via ammonium or hydroxonium ions, one-site or multiple-site hopping of the hydrogen nuclei, or a homolytic decomposition of the Brønsted site provides the dominant contribution to the proton mobility in the zeolite. The present ^{1}H MAS NMR studies of H-Y and H-ZSM-5 include a wide range of measuring temperatures between 160 and 790 K, a temperature range of zeolite activation between 570 and 723 K, and a weak reammoniation or rehydration of the zeolites, to gain insight into the nature of the proton mobility under various conditions.

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2. Experimental

Zeolite Y (Si/Al = 2.4, 85% NH_4^+ and 15% Na^+) was donated by UOP. Zeolite ZSM-5 (Si/Al = 13.2, 100% NH_4^+) was template-free synthesized and donated by TRICAT. Si/Al ratios were determined by ^{29}Si and ^{27}Al MAS NMR. The ammonium forms were converted to the hydrogen forms by the following activation procedure. All samples were pretreated by heating 6-mm-deep layers of zeolite in glass tubes (3 or 5 mm o.d.) at a rate of $10\ K\,h^{-1}$ under vacuum. After maintaining the samples at the activation temperature (570–723 K) under a pressure (in the sample) of <1 Pa for 24 h, the samples were cooled to room temperature and then sealed. In some cases, before sealing they were partially loaded under vacuum with a small amount of ammonia or water molecules. After an activation procedure at 673 K, the zeolite H-Y contained 6.0 bridging hydroxyl groups per cavity (1/8 unit cell), whereas the zeolite H-ZSM-5 had 1.7 bridging hydroxyl groups per crossing (1/4 unit cell). This was verified by comparing the intensities of the signals in the ^1H MAS NMR spectra with those of a well-characterized reference sample [9]. Zeolite deuteration was performed by contact with 3 kPa D_2O at 673 K for 30 min, followed by evacuation. This procedure was repeated 5 times, followed by a final evacuation at 673 K for 12 h. A bridging hydroxyl group H/D exchange of 90% and 95% for zeolites H-Y and H-ZSM-5, respectively, was obtained. The zeolites were not harmed by the exchange procedure, as demonstrated by ^{29}Si and ^{27}Al MAS NMR spectroscopy.

^1H MAS NMR spectra of the sealed samples were recorded at 300 MHz (laser experiments) or at 400 MHz and spinning rates of 1 (laser experiments), 3, or 4 kHz. The MAS probe with the 50-W-CO_2-laser has been described previously [10]. Temperature calibration was done by ^{207}Pb MAS NMR spectroscopy of $Pb(NO_3)_2$ [11]. A Hahn echo with pulse spacing of one rotation period and a 16-phase cycle was used to measure the ^1H MAS NMR spinning side band spectra. The BRUKER program WINNMR was used for data processing. A Lorentzian fit of the spinning side bands yielded the *fwhm* (full width at half maximum) of the envelope, denoted by $\delta\nu_{1/2}$, whereas the *fwhm* of the center signal was obtained by a Lorentzian/Gaussian fit of one, two, or three signal components, designated the "line width."

One-dimensional ^1H NMR exchange spectroscopy (EXSY) of ammonia-loaded zeolites H-Y was performed using a NOESY pulse group. The development time between the first and second pulses was adjusted to $t_1 = 1/4\Delta\nu$, where $\Delta\nu$ denotes the distance between the two signals of ammonium and bridging OH groups. The MAS frequency corresponds to multiples of $\Delta\nu$. Two series of dependencies of the mixing time, t_m, between the second and third pulses were measured. For series one, the offset was shifted by $\Delta\nu$ from the left side of the left signal (ammonium ions). For series two, the offset was shifted by $\Delta\nu$ to the right side from the right signal (bridging hydroxyl groups). Each series exhibited one (hydroxyl or ammonium) signal as the diagonal peak and the other signal as the cross peak (Fig. 3). A fit of the obtained data gives the longitudinal relaxation time T_1 and the exchange times [12].

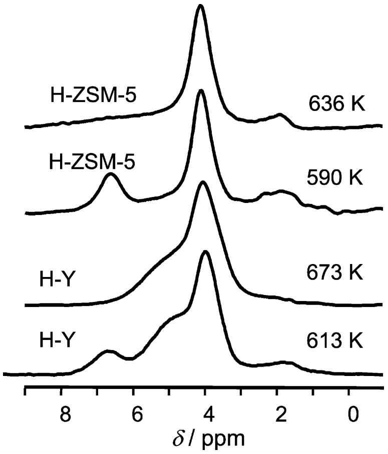

Fig. 1. Room-temperature ^1H MAS NMR spectra of zeolites H-ZSM-5 and H-Y pretreated at temperatures between 590 and 673 K.

3. Results

Typical ^1H MAS NMR spectra of the activated zeolites are shown in Fig. 1. It is well known [13] that these spectra consist of several signals. A component of the signal in the range 0.5–2.5 ppm is due to nonacidic SiOH (silanol) groups at framework defects and in amorphous parts of the sample. For H-Y zeolites, the signals of bridging (structural) hydroxyl groups are found at 3.9 ppm (due to bridging OH groups pointing into the large zeolite cages) and 4.9 ppm (due to bridging OH groups pointing into the sodalite cage, a signal shoulder in Fig. 1). Comparison of intensity with a reference sample demonstrates that the used zeolite H-Y has a total of 6 OH p.c. Four of these hydroxyls are located on O1 positions (giving rise to the signal at 3.9 ppm), and two are located on O3 positions (giving rise to the signal at 4.9 ppm). For zeolite H-ZSM-5, a narrow signal component at 4.2 ppm corresponds to bridging hydroxyl groups, which are fixed at a single oxygen atom, and a broad component at 6.0 ppm (broad shoulders in Fig. 1) corresponds to bridging hydroxyls exchanging between several oxygen positions [9]. A signal at about 7 ppm can be assigned to residual ammonium cations. The latter can be found in spectra of ammonium forms of zeolites, which are activated at temperatures significantly below the commonly used activation temperature of 673 K.

Fig. 2 shows some room-temperature ^1H MAS NMR spectra of zeolites H-ZSM-5 and H-Y that were pretreated at 673 K and then loaded with ammonia molecules. The spectra exhibit a signal at 6.9 ± 0.1 ppm due to the ammonium cations formed by the reaction of the loaded ammonia molecules with bridging hydroxyls. This results in a zeolite similar to that without ammonia loading and activation temperature below 623 K. Fig. 2 also shows the first spinning side bands. It can be seen that the ammonium signal has no spinning side bands. The ions are very mobile, and the dipolar interaction of the ^1H nuclei with the ^{27}Al nuclei of the framework is averaged out by the mobility.

Fig. 3 shows an example of one-dimensional EXSY. Table 1 presents some kinetic parameters were obtained by fitting the intensities as functions of the mixing time (solid lines in Fig. 3)

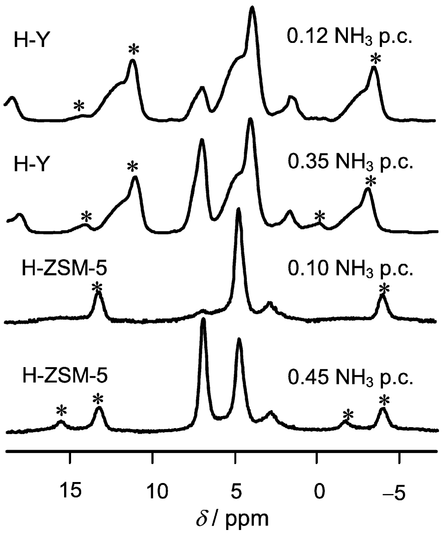

Fig. 2. Room-temperature ^{1}H MAS NMR spectra of zeolites H-ZSM-5 and H-Y pretreated at 673 K and loaded with less than one ammonia molecule per cavity or per crossing. Asterisks denote the first spinning side bands.

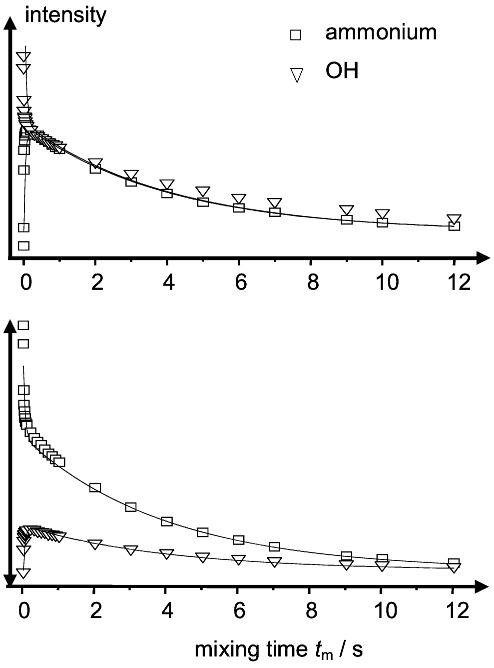

Fig. 3. ^{1}H MAS NMR signal intensity of ammonium and OH groups in dependence on the mixing time t_m. The zeolite H-Y was loaded with 1.5 ammonia molecules per cavity. The measurements were performed at 360 K. The figures on the top and bottom correspond to offset on the left-hand side and right-hand side of the signals, respectively.

for three temperatures and three ammonia loadings. Because the obtained values of T_1 did not differ significantly for ammonium ions and hydroxyl groups, we finally used a fitting procedure with only one value for $T_1 = T_{1\text{OH}} = T_{1\text{ammonium}}$. Here τ_{ammonium} and τ_{OH} denote the mean residence time (before the exchange takes place) of a hydrogen atom in one ammonium ion and one bridging hydroxyl group, respectively. The exchange rate is defined as $k = (1/\tau_{\text{ammonium}} + 1/\tau_{\text{OH}})$. Under the given equilibrium conditions, we have $n_{\text{OH}}/\tau_{\text{OH}} = n_{\text{ammonium}}/\tau_{\text{ammonium}}$ with n_{ammonium} and n_{OH} as the concentrations of hydrogen atoms in ammonium ions and hydroxyl groups, respectively. It follows that $k = 1/\tau_{\text{OH}} \times (n_{\text{ammonium}} + n_{\text{OH}})/n_{\text{ammonium}} = (1/\tau_{\text{ammonium}} \times (n_{\text{ammonium}} + n_{\text{OH}})/n_{\text{OH}})$. The application of this equation to the values in Table 1 gives concentrations of hydroxyl groups in the range of 2.8–5.6 OH groups per cavity (mean, 4 OH groups per cavity). For the used zeolite H-Y, we previously found (see the first paragraph of this section) a total of 6 OH p.c., four of which are located on O1 positions (giving rise to the signal at 3.9 ppm), with the other two located on O3 positions (giving rise to the signal at 4.9 ppm). The resolution of the two corresponding signals is very low at a MAS frequency of about 4 kHz; it can be improved by using MAS frequencies above 10 kHz [9].

Table 1

Longitudinal relaxation times T_1, mean residence times τ, and exchange rates k obtained by ^{1}H MAS NMR with one-dimensional EXSY on ammonia loaded zeolites H-Y in dependence on the temperature

Temperature (K)	Molecules p.c.	T_1 (s)	τ_{OH} (s)	τ_{ammonium} (s)	k (s^{-1})
297	1.5 NH_3	4.0	0.30	0.65	4.9
	0.35 NH_3	6.0	2.2	0.60	2.1
	0.1 NH_3	10.0	6.0	0.65	1.7
360	1.5 NH_3	4.0	0.08	0.17	18.4
	0.35 NH_3	6.0	0.60	0.16	7.9
370	1.5 NH_3	3.0	0.05	0.10	30.0
	0.35 NH_3	6.0	0.40	0.10	12.5
	0.1 NH_3	6.0	1.00	0.10	11.0

It is remarkable that the mean residence time τ_{ammonium} of a hydrogen atom in an ammonium ion does not vary if the ammonia-loading increases from 0.1 to 1.5 molecules per cavity (see Table 1). We measured 0.10 s at 360 K and 0.16–0.17 s at 370 K, giving an apparent activation energy of 50 ± 10 kJ mol^{-1}. (We did not include data obtained at room temperature, because they seem to be influenced by spin diffusion rather than by mobility of the nuclei.) Extrapolating this temperature dependence, we obtain $\tau_{\text{ammonium}} = 0.2$–2 ms for 540 K.

It should be noted here that apparent activation energies obtained from NMR data are of low accuracy, for one main reason. It is always accepted that only a single mechanism is broadening the line or causing an exchange; unfortunately, however, in many cases two mechanisms are superimposed.

Fig. 4 and Tables 2 and 3 present temperature-dependent results of ^{1}H MAS NMR spectroscopy of ammonia-loaded zeolites. The *fwhm* of the spinning sideband envelope is denoted by $\delta\nu_{1/2}$ (Lorentz fit), whereas "line width" corresponds to the *fwhm* of signals (Gauss/Lorentz fit) in the center band. The figure and the tables show that the signals of bridging hydroxyl groups and ammonium ions merge above 400 K. If more than one ammonia molecule per cage or per crossing is loaded, then merging occurs at 360 K [14]. The line merging provides information about the proton-exchange dynamics. An ideal merging without MAS is easily simulated and results in a narrow line at the center of gravity of the merging signals [15], but this is not the case for the samples under study. Fig. 4 and Table 2 correspond (per cavity) to 0.6 ammonium ions or 2.4 hydro-

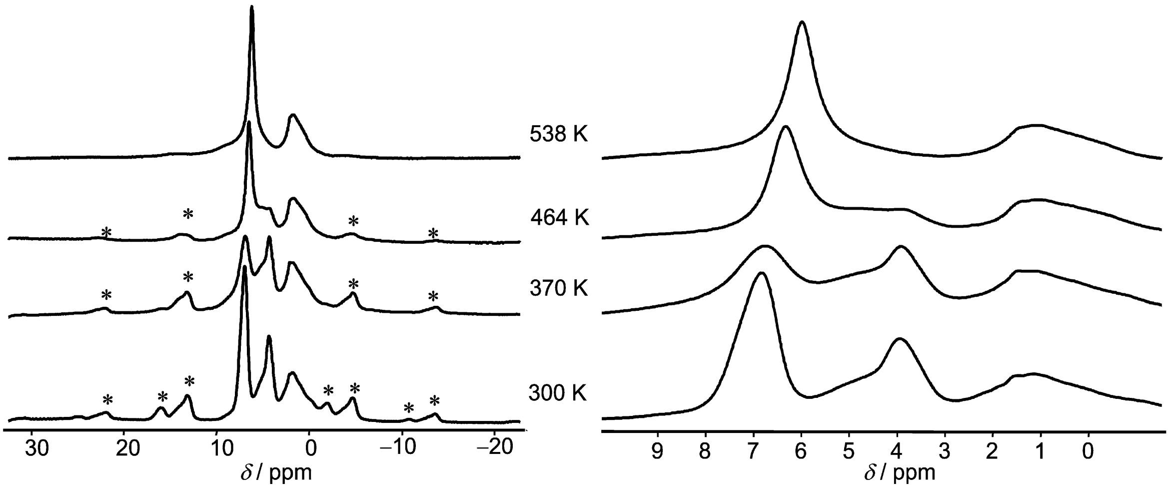

Fig. 4. Temperature dependence of ^{1}H MAS NMR spectra of the zeolite H-Y activated at 673 K and loaded with 0.6 NH_3 molecules per cavity.

Table 2
Temperature-dependent NMR parameters obtained from the ^{1}H MAS NMR spectra of the zeolite H-Y activated at 673 K and loaded with 0.6 NH_3 molecules per cavity

	300 K	370 K	464 K	538 K
$\delta\nu_{1/2}$ NH_4^+ (Hz)	2800	1500	–	–
$\delta\nu_{1/2}$ OH (Hz)	5000	4500	4300	–
Linewidth NH_4^+ (Hz)	410	630	390	340
Linewidth OH (Hz)	800/410	630/380	640/390	–
Position NH_4^+ (ppm)	7.1	7.0	6.5	6.1
Position OH (ppm)	5.0/3.9	5.0/3.9	5.0/3.9	–

Table 3
Temperature-dependent NMR parameters obtained from the ^{1}H MAS NMR spectra of the zeolite H-ZSM-5 activated at 673 K and loaded with 0.45 NH_3 molecules per crossing

	300 K	368 K	458 K	550 K
$\delta\nu_{1/2}$ NH_4^+ (Hz)	2500	1800	–	–
$\delta\nu_{1/2}$ OH (Hz)	4600	4200	–	–
Linewidth NH_4^+ (Hz)	230	180	490	1360
Linewidth OH (Hz)	340/1300	1020/1250	590/430	–
Position NH_4^+ (ppm)	6.9	6.9	7.0	5.2
Position OH (ppm)	4.3/6.0	4.6/6.6	4.7/5.8	–

gen nuclei in ammonium ions (7.1 ppm), about 1.8 hydrogen atoms in O3H groups (5.0 ppm), and about 3.6 hydrogen atoms in O1H groups (3.9 ppm). The ideal merging would be expected at 5.1 ppm, but the experimentally obtained value is 6.1 ppm (see Table 2). This indicates that not all bridging hydroxyl groups are involved in the merged signal, and we cannot properly simulate the exchange. Nevertheless, to estimate the exchange time, we use the simplest model of two signals with identical intensities and exchange times τ and the distance of $\Delta\nu$, which merge to one signal in the middle. The coalescence temperature is defined as the temperature at which we observe the transition from two maxima to one (broad) maximum of the spectrum. The exchange time τ at the coalescence temperature amounts to $\tau = 1/(2\pi\Delta\nu)$ [15]. This exchange time means that all four hydrogen nuclei are transferred from one ammonium ion to bridging hydroxyl groups. For a loading of 0.6 ammonia molecules per cage in zeolite H-Y and a signal distance of 3.2 ppm (1280 Hz) between O1H groups and ammonium molecules, we obtained $\tau = 124$ µs at a coalescence temperature of about 540 K. From EXSY (see the previous paragraph), we obtained by extrapolation for the mean residence time of one hydrogen atom in the ammonium ion $\tau_{\text{ammonium}} = 0.2$–2 ms for 540 K. The difference is quite large if we take into consideration that in our model, the exchange of the four hydrogen nuclei of the ammonium ion takes much longer than the exchange of only one atom. Thus, we cannot verify that the merging of the ammonium and hydroxyl signals in ammonia-loaded zeolites H-Y at higher temperatures (540 K) is caused by a hydrogen exchange between O1H groups and ammonium ions. For ammonia-loaded H-ZSM-5, the merging of ammonium and hydroxyl signals can be observed at temperatures 50 K lower than those for H-Y [14]. Finally, we note again that the samples rotate with 3–4 kHz. Exchange rates near this frequency have a corruptive influence on the line narrowing by MAS and cause a line broadening, which is superimposed on the exchange broadening of the simple two-site model [15]; see Section 4.

Spinning sideband envelopes of the ammonium ion signals were measured to study the narrowing of the *static* ammonium line shapes of ^{1}H and ^{2}H NMR in the temperature range 170–500 K. Note that the intrinsic ^{1}H NMR "static" linewidth of an isolated ammonium ion amounts to 74 kHz [14]; this value can be halved by rotation around one axis. First-order quadrupolar broadening dominates the line widths of the ^{2}H NMR spectra. We would expect an intrinsic "static" linewidth of 118 kHz and a value of 39 kHz for rotation around one axis [14]. Fig. 5 shows the *fwhm* of the spinning side band envelope of the ^{1}H MAS NMR spectra of the zeolite H-Y loaded with 0.6 ammonia molecules per cavity. The observed temperature-independent static linewidth $\delta\nu_{\text{rigid}}$ equals 3.2 kHz. Fig. 6 shows the corresponding values of the ^{2}H MAS NMR spectra ($\delta\nu_{\text{rigid}} = 17$ kHz) of the deuterated zeolite H-ZSM-5 loaded with 0.33 ammonia molecules per crossing. The dashed lines on the left can be explained by apparent activation energies in the range of 25–45 kJ mol^{-1}. The slopes of the dashed

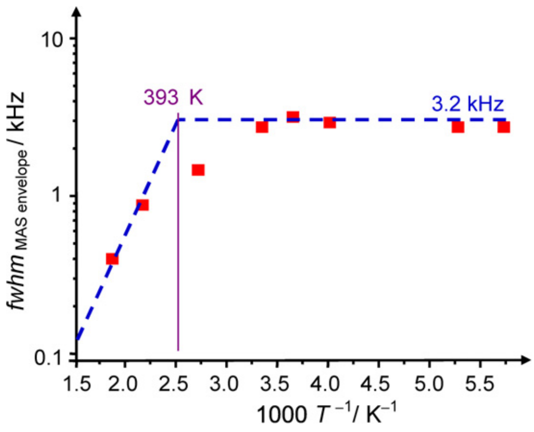

Fig. 5. *fwhm* of the spinning side band envelope of the ^{1}H MAS NMR spectra of the zeolite H-Y loaded with 0.6 ammonia molecules per cavity.

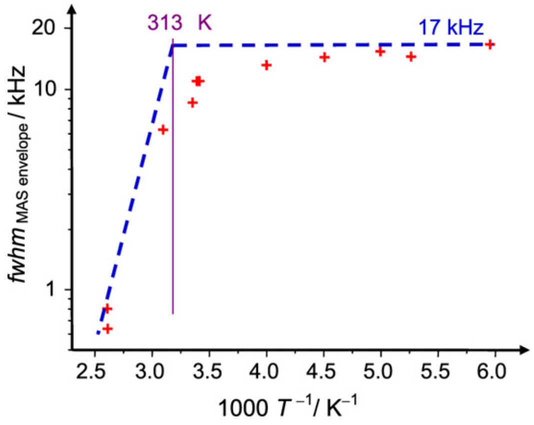

Fig. 6. *fwhm* of the spinning side band envelope of the ^{2}H MAS NMR spectra of the deuterated zeolite H-ZSM-5 loaded with 0.33 ammonia molecules per crossing.

lines on the left side are not sufficiently stated by the experimental points, but the onset of line narrowing (i.e., crossing of the dashed lines) is well defined by the experimental points, if we take into account that the experimentally obtained linewidth on the onset should be half the value of the static line width $\delta\nu_{\text{rigid}}$ [16].

The NMR correlation time is defined as the time increment of a mono-exponential decay of the nuclear interaction. But the correlation time is equal to the mean residence time of the nucleus on one site for intersite hopping of hydrogen nuclei in a zeolite [16]. The NMR correlation time, τ_c, at the temperature of the onset of line narrowing can be obtained (in the case of a Lorentzian line shape cutoff at 10 times the *fwhm*) by the equation $\tau_c = 1/(15.3\delta\nu_{\text{rigid}})$ [14,16]. From Figs. 5 and 6 (and a similar temperature dependence of the 2H NMR of zeolite H-Y loaded with 0.26 ammonia molecules per cavity [14]), we obtain $\tau_c = 4.7$ µs at 323 K for ^{2}H NMR of H-Y, 20.4 µs at 393 K for ^{1}H NMR of H-Y, and 3.8 µs at 313 K for ^{2}H NMR of H-ZSM-5.

Now the question arises as to how the obtained magnetic resonance correlation time, τ_c, is connected to parameters describing the mobility of the ammonium ions. The broadening of the ammonium line shape is at low temperature dominated by dipolar interaction and quadrupolar interaction for ^{1}H NMR and ^{2}H NMR, respectively. Rotation of the ammonium ion around one of the three C3-axes reduces the (intra-ion) homonuclear dipolar interaction and the quadrupolar interaction. Free rotation around all axes averages this dipolar interaction to zero and dramatically reduces the quadrupolar interaction. A detailed consideration is given in [14]. Along with homonuclear interactions, we have heteronuclear dipolar interactions between the hydrogen nuclei of the ammonium ion and the aluminum nuclei of the zeolite framework. Previously, it was calculated that two aluminum nuclei in a six-oxygen ring of the zeolite Y with a distance of 3.133 Å to the center of the ammonium ion cause a line broadening of 4.9 kHz in the ^{1}H ammonium spectrum [14]. A stronger broadening of the ^{2}H NMR spectra results from the fact that even for freely rotating ions in one six-ring, there remains a field gradient along the symmetry axis of the ring that causes a quadrupolar broadening of the signal.

Consequently, the aforementioned correlation time should be connected with ammonium ion jumps between several oxygen rings of the framework. At 170 K (the minimum measurement temperature) and above, the rotation axis of the ion located on one oxygen ring is subjected to a multiple reorientation, but the ion remains on the ring containing the negatively charged AlO_2-ions. Above room temperature, the ion jumps between several oxygen rings of the framework; for example, for the zeolite H-Y loaded with 0.6 ammonia molecules per cavity, we have a mean residence time of about 20 µs at 393 K on one oxygen ring.

Fig. 7 (right side) shows the temperature-dependent spectra of a weakly rehydrated zeolite H-ZSM-5. The spectrum evaluation is more difficult for weakly rehydrated samples (compared with weakly reammoniated samples), because a separated signal of the water species is not seen. (For a stronger rehydrated sample, 1 H_2O p.c., a signal of gaseous water molecules at 0.3 ppm can be observed above 400 K [14].) The weak signal at 6.3 ppm, which is superimposed on the room-temperature spectrum of the dehydrated zeolite H-ZSM-5 (see Fig. 7, left side) can be explained by hydrogen nuclei that undergo a rapid exchange between water molecules and hydroxonium ions [17]. The weak water loading causes broadening of the signals. The *fwhm* of the bridging hydroxyl signal at 4.2 ppm increases from 245–365 Hz in the temperature range 297–553 K to 540–1780 Hz for the slightly rehydrated sample.

Two effects can contribute to the observed line broadening of 1–2 kHz: chemical exchange and a corruptive affect of mobility on MAS narrowing. Reaction or jump rates should be on the order of magnitude of kHz. The important conclusion that can be drawn from Fig. 7 and Table 4 is that a small amount of water molecules in zeolite H-ZSM-5 increases the mobility of bridging hydroxyl groups, as reflected in the temperature dependence of the ^{1}H MAS NMR spectra.

Now we compare the weakly reammoniated or rehydrated samples with those activated under vacuum at different temperatures between 573 and 723 K [18]. The latter still contained residual amounts of water or ammonium ions in the zeolitic crystallites. They were investigated by ^{1}H MAS NMR with a 3-kHz rotation frequency and conventional heating at room

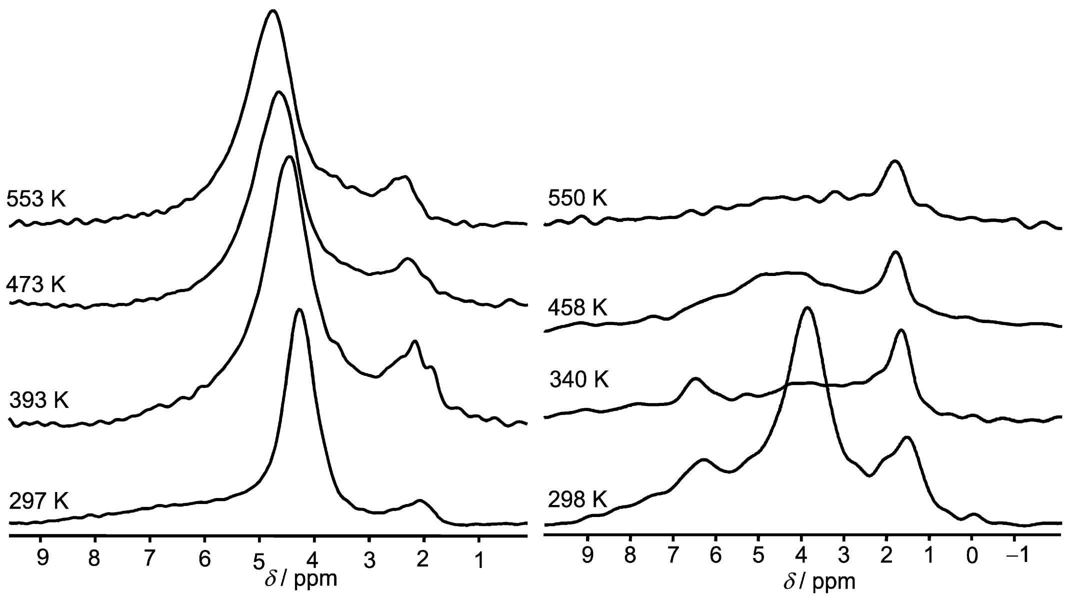

Fig. 7. Temperature dependence of ^{1}H MAS NMR spectra of zeolite H-ZSM-5 activated at 673 K. The spectra on the left and right side correspond to the dehydrated zeolite and to the zeolite which was loaded with 0.33 H_2O molecules per crossing, respectively.

Table 4
Temperature-dependent NMR parameters obtained from the ^{1}H MAS NMR spectra of the zeolite H-ZSM-5 activated at 673 K. The parameters on the left and right side correspond to the dehydrated zeolite and to the zeolite which was loaded with 0.33 H_2O molecules per crossing, respectively

	Dehydrated				Loaded with 0.33 H_2O molecules p.c.			
	298 K	393 K	473 K	553 K	298 K	340 K	458 K	550 K
$\delta\nu_{1/2}$ (Hz)	5023	3790	3151	2466	4000	4600	–	–
Position (ppm)	4.2/5.3	4.5/5.3	4.7/5.4	4.8/5.5	3.9/6.3	3.6/6.5	4.4	3.7
Linewidth (Hz)	245/599	360/417	365/479	365/468	540/530	1600/433	1670	1780

temperature up to 553 K and laser heating and a 1-kHz rotation frequency between 554 and 773 K. The activation temperature was set at 573–723 K for two reasons: (i) zeolites activated below 573 K contain excessive concentrations of residual water molecules and ammonium ions, and (ii) above 723 K, hydrogen forms of zeolites can be destroyed.

Note that no significant differences were found in the signal intensities of hydroxyl groups for activation temperatures in the range 573–723 K. The intensities can be measured with an accuracy of ±10%. With this limitation, we found no decrease in the concentrations of hydroxyl groups with increasing activation temperature in this temperature range.

Fig. 8 shows a typical ^{1}H MAS NMR temperature dependence up to 553 K obtained for the zeolite H-ZSM-5 activated at 610 K. The spectra of zeolites H-ZSM-5 exhibit an ammonium signal up to the activation temperature of 610 K, whereas this signal is not seen in all of the spectra of zeolite H-Y activated at 570 K and above. The amounts of residual ammonium ions per crossing are 0.3 at 570 K, 0.13 at 590 K, and 0.08 at 610 K, indicating that the amount is halved by a 20-K increase in activation temperature. For zeolites H-Y activated at 570 K and above and for zeolites H-ZSM-5 activated at 636 K and above, the residual concentration of ammonium ions is lower than 1 ion per 30 cavities and crossings, respectively. This corresponds to our detection limit. Fig. 8 and Table 5 show that the spectra of samples containing residual ammonium ions exhibit stronger broadening of the 4.2-ppm line when the measuring temperature is increased from 300 to 553 K. Fig. 8 also shows that ammonium and bridging hydroxyl signals merge above 400 K. The spectra appear similar to those measured on a zeolite H-ZSM-5 activated at 673 K and loaded with 0.1 ammonia molecule per crossing [14]. For both zeolites, the line broadening and merging above 400 K is linked to the hydrogen exchange between bridging hydroxyls and ammonium ions.

For zeolites H-ZSM-5 activated at 636 K and above, we see no significant differences in the spectra in terms of dependence on activation temperature. For the 4.2-ppm line, the *fwhm* of the line increases by a factor of about 1.5, and the *fwhm* of the spinning sideband envelope decreases by a factor of about 0.5 with an increase in measuring temperature from 300 K to 553 K (see Table 5). The shift of the signal maxima increases by about 0.5 ppm. These effects can be explained by a chemical exchange of bridging hydroxyl groups between the sites, giving rise to the 4.2- and 6.0-ppm signals. We assume that the concentration of residual water molecules or ammonium ions (<0.03 ions p.c. at an activation temperature of 636 K) is reduced significantly with increasing activation temperature, as mentioned above; therefore, we conclude that these residual species are not important for the hydrogen mobility in the H-ZSM-5 samples, which were activated at 636–711 K.

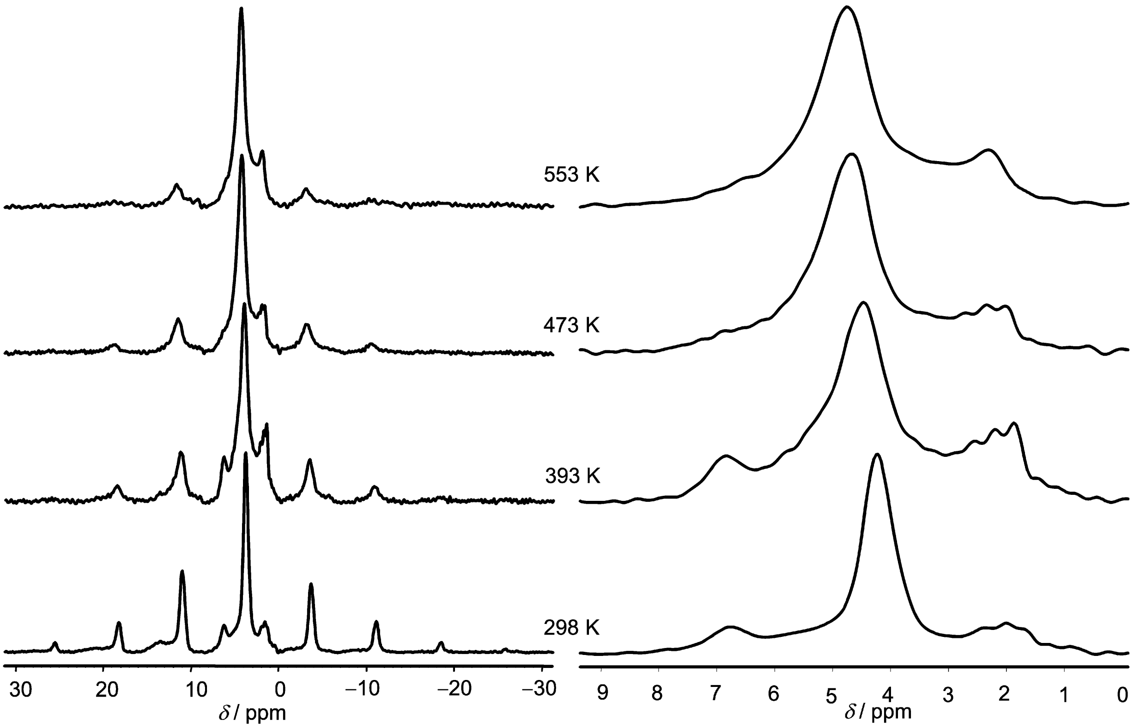

Fig. 8. Temperature dependence of ^{1}H MAS NMR spectra of zeolite H-ZSM-5 activated at 610 K. The residual ammonium concentration amounts to 0.08 ions per crossing.

Table 5
Temperature-dependent NMR parameters obtained from the ^{1}H MAS NMR spectra of the zeolites H-ZSM-5 activated at temperatures in the range 570–711 K and measured at 300 K and at 553 K. The parameter $\Delta\delta$ denotes the difference of the chemical shift of the maximum peak in the spectra measured at 300 and at 553 K

Activation temperature (K)		570	590	610	636	656	677	711
$\delta\nu_{1/2}$ OH (kHz)	300 K	5.08	4.98	4.97	5.14	5.11	5.02	5.07
	553 K	2.79	2.28	2.48	2.31	2.47	2.47	2.33
Line width OH (Hz)	300 K	245	245	257	245	257	245	241
of the 4.2-ppm-line	553 K	639	531	421	394	365	365	342
$\Delta\delta$ (ppm)		0.7	0.6	0.5	0.5	0.5	0.5	0.6

Table 6
Temperature-dependent NMR parameters obtained from the ^{1}H MAS NMR spectra of the zeolites H-Y activated at temperatures in the range 570–673 K and measured at 300 K and at 553 K. The parameter $\Delta\delta$ denotes the difference of the chemical shift of the maximum peak in the spectra measured at 300 K and at 553 K

Activation temperature (K)		570	590	610	630	650	673
$\delta\nu_{1/2}$ OH (kHz)	300 K	6.03	6.03	5.93	6.03	5.94	6.05
	553 K	4.77	4.52	4.68	4.75	4.61	4.66
Line width OH (Hz)	300 K	400	331	354	314	320	360
of the 3.9-ppm-line	553 K	542	565	502	485	479	513
$\Delta\delta$ (ppm)		0.2	0.2	0.4	0.4	0.4	0.2

Table 6 shows the corresponding data for the zeolite H-Y. The data do not vary significantly with activation temperatures in the range 570–673 K and change only slightly at measuring temperatures in the range 300–553 K. For the 3.9-ppm line, the *fwhm* of the line increases by a factor of about 1.5 and the *fwhm* of the spinning sideband envelope decreases by a factor of about 0.77 at 553 K compared with those at 300 K. The chemical shift of the spectrum maxima increases by 0.3 ± 0.1 ppm. Note that the bridging hydroxyl signal can be deconvoluted into two lines with a distance of 1 ppm up to the measuring temperature of 553 K [18]; thus, a hydrogen exchange between the two sites cannot be observed in these spectra of zeolites H-Y.

Fig. 9 shows typical temperature-dependent spectra obtained by laser heating at a 1-kHz rotation frequency. The line width $\delta\nu_{1/2}$ in the Arrhenius plot denotes the *fwhm* of the spinning sideband envelope or of the unresolved signal if spinning sidebands are not resolved. Note that after measuring of the sample at 773 K, we performed an additional measurement at room-temperature. We did not make use of spectra if the room temperature spectrum after laser heating differed from the room-temperature spectrum obtained before heating.

We again use the rule that the experimental point should have half the value of the rigid one at the temperature of the onset of narrowing, to fit the temperature-dependent straight line to the experimental points. Table 7 presents the results of the 8 samples under study (zeolites H-Y and H-ZSM-5 activated at four different temperatures). The apparent activation energy of the Arrhenius plot differs slightly at the different activation temperatures for the zeolite H-Y. For the zeolite H-ZSM-5, the differences are significant. The important point is that only very small changes in temperature of the onset of narrowing were

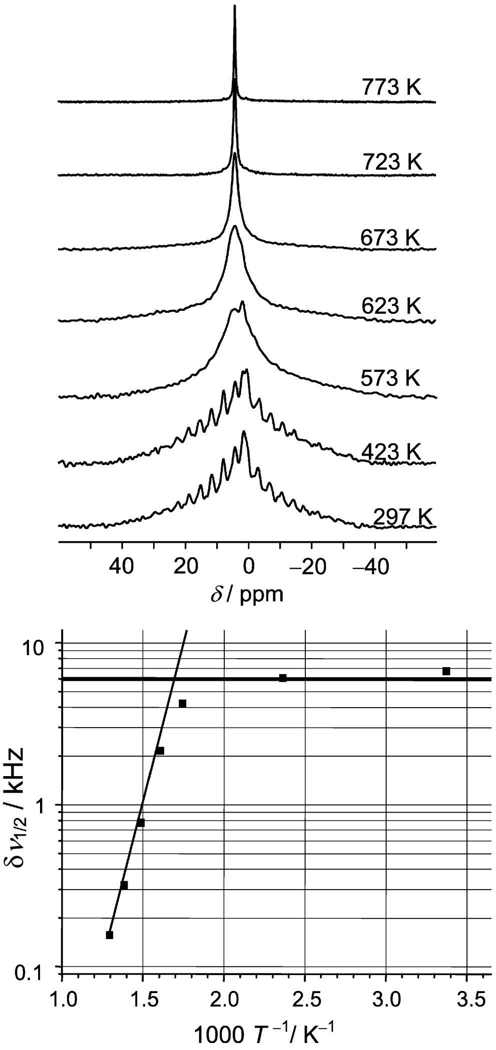

Fig. 9. Spectra and Arrhenius plot of the temperature dependent ^{1}H MAS NMR measurements which were obtained by laser heating. The zeolite sample H-Y was activated at 673 K.

Table 7
Energies obtained from the slopes in the Arrhenius plots and narrowing-onset-temperatures obtained from the intersection of the two straight lines in the Arrhenius-plots; see Fig. 9

Activation temperature (K)		573	623	673	723
Zeolite H-Y	Energy (kJ mol^{-1})	66.7	55.8	76.6	53.5
	Narrowing onset (K)	532	521	592	526
Zeolite H-ZSM-5	Energy (kJ mol^{-1})	40.9	33.5	23.0	17.3
	Narrowing onset (K)	515	508	481	426

seen in all samples. At the temperature of the onset of narrowing, we find correlation times of $\tau_c = 73$ and 88 µs for the zeolites H-Y and H-ZSM-5, respectively, from the *fwhm* in the rigid region.

Ernst et al. [4] obtained similar spectra of samples activated at 723 K. They found apparent activation energies of 78 kJ mol^{-1} for H-Y and 18 kJ mol^{-1} for H-ZSM-5, similar to our sample H-Y activated at 673 K and sample H-ZSM-5 activated at 723 K.

When discussing the obtained correlation times τ_c, we need to take into consideration that a line narrowing occurs from 6 kHz to 150 Hz for H-Y and from 5 kHz to 500 Hz for H-ZSM-5. MAS reveals no significant narrowing at higher temperatures, because spinning sidebands are not observed. Dipolar proton–proton interaction, dipolar proton–aluminum interaction, and anisotropy of the chemical shift (about 15 ppm [13]) can be averaged out by the proton jumps, which give rise to the correlation time τ_c. Thus, the foregoing line narrowing should be connected with ^{1}H jumps between bridging hydroxyl sites in several oxygen rings of the zeolitic framework.

4. Discussion

^{1}H NMR spectroscopy shows the intersite hydrogen motion between different aluminum sites in the framework. In our first study in 1974 [1], we explained the results by one-site jumps among the four oxygen atoms around one aluminum atom. But three years later [19], we corrected this incorrect explanation, and in another, more recent study [4], we proposed that intersite jumps are superimposed on one-site jumps. A strong argument for intersite jumps is the drastic line narrowing seen. The dominating contribution to the line broadening comes from the dipolar proton–aluminum interaction. In principle, this can be averaged out by one-site jumps if the jumps occur among tetrahedral arranged sites with an equal probability of occupation. But the latter condition is not fulfilled for H-forms of zeolites in particular. For example, zeolites H-Y contain structural hydroxyl groups on O1 and O3 positions. Jumps between all four positions will decrease the proton–aluminum line broadening by half only if a dominant occupation of two positions occurs. Thus, a line narrowing by one order of magnitude or greater should be explained by intersite hydrogen motion between different aluminum sites in the framework.

Later, we will return to the topic of the previous paragraph. Now we discuss the influence of small amounts of ammonium ions or water molecules on the proton mobility. Our temperature-dependent ^{1}H MAS NMR studies of ammonia-loaded zeolites have shown that the ammonium ions are very mobile. At temperatures above 168 K, they perform several reorientations around all symmetry axes within a time interval of 30 µs. But they remain on one oxygen ring of the zeolitic framework despite the isotropic rotations at low temperatures. However, jumps between multiple oxygen rings can be observed above 300 K. For the zeolite H-Y loaded with 0.6 ammonia molecules per cavity, we found a mean residence time of 20 µs at 393 K for the ammonium ion in one oxygen ring.

The main, but not unexpected, result of the EXSY on ammonia-loaded zeolites Y is that the mean residence time, τ_{ammonium}, of the hydrogen nuclei in one ammonium ion does not depend on the amount loaded. We obtained $\tau_{\text{ammonium}} =$ 0.10 s at 370 K and 0.16–0.17 s at 360 K. An apparent activation energy of 50 ± 10 kJ mol^{-1} was determined between the two temperatures. Extrapolation to 393 K gives $\tau_{\text{ammonium}} =$ 40 ms.

An important and unexpected result comes from comparing the mean residence time of the ammonium ion in one oxygen ring (20 µs at 393 K) with the exchange time (40 ms at 393 K). This means that the ammonium ion jumps 2000 times between multiple sites before a hydrogen exchange with bridging hydroxyl groups occurs. The model for this is as follows: After 2000 jumps as an ammonium ion, the ion leaves one hydrogen atom on an oxygen atom of the framework and jumps once as an ammonia molecule to another bridging hydroxyl, forming a ammonium ion once again. This is contrary to an previous claim by Simon et al. [7,20] that ammonia acts only as a solvent and remains in the state of a molecule. But Franke and Simon proved in a more recent study [8] that, depending on temperature and degree of ammonia loading, a mechanism involving ammonium ions as well as reorientation movement is involved in proton conductivity.

The coalescence of two lines that are well resolved at lower temperature (i.e., slow chemical exchange) to a single broad line at higher temperature (i.e., medium chemical exchange) can be described most simply by a two-site model. The two signals with identical intensities and the frequency distance of $\Delta\nu$ merge by fast chemical exchange to a single narrow signal in the middle. The exchange time, τ, at the coalescence temperature (i.e., medium chemical exchange) amounts to $\tau = 1/(2\pi\Delta\nu)$, see [15, p. 80].

A different effect with similar results is the influence of the correlation time τ_c on the broadening of MAS signals at an angular rotation frequency of ω_{rot}. A maximum value of the *fwhm*, $\delta\nu_{1/2}$, can be found for $\tau_c \approx 1/\omega_{rot}$. Andrew and Jasinski [21] introduced the equation

$$\delta\nu_{1/2}^{MAS} = \frac{M_2}{3\pi}\left[\frac{2\tau_c}{1+(\omega_{rot}\tau_c)^2} + \frac{\tau_c}{1+(2\omega_{rot}\tau_c)^2}\right],$$

where M_2 denotes the second moment of the NMR line shape.

Baba et al. [3,22–24] studied hydrogen zeolites at temperatures up to 473 K and analyzed the line broadenings (by a factor of about two) using the foregoing equation. We found similar line broadenings in this small temperature range. But there is a problem with the application of this equation. The equation predicts for $\tau_c \gg 1/\omega_{rot}$ (i.e., for a low temperature at which spinning sidebands can be observed [room temperature]) a line narrowing proportional to the square of the rotation frequency. Going from 3.8 to 12 kHz, the value $\delta\nu_{1/2}$ should be reduced by a factor of 0.1. We observed no such drastic narrowing with increasing MAS frequency. The explanation for this discrepancy is simple. Bridging hydroxyl signals are broadened mainly by a distribution of isotropic values of the chemical shift, which is not included in the foregoing equation. Nonetheless, the equation can be used to demonstrate qualitatively the maximum line broadening for $\tau_c \approx 1/\omega_{rot}$. The simple coalescence model gave a maximum broadening for $\tau \approx 1/\Delta\omega$. Both effects are superimposed for our studies. The chemical shift differences and MAS rotation frequencies are (in angular frequencies) on an order of magnitude of $10^4\ s^{-1}$; therefore, both effects cause a maximum broadening for exchange times or correlation times on an order of magnitude of 100 µs.

This rough estimation of a kinetic parameter is helpful for the analysis of some temperature-dependent ^{1}H MAS NMR spectra. The weakly rehydrated H-ZSM-5 shown in Fig. 7 demonstrates, in addition to the temperature-independent signal of silanol groups at about 1.5 ppm, a signal of bridging hydroxyl groups at about 4 ppm and a signal due to hydroxonium species at about 6.5 ppm. At 340 K, the signal of bridging hydroxyl groups disappears due to mobility that can be roughly estimated based on correlation time on an order of magnitude of 100 µs. At 458 K, the signal at 6.5 ppm disappears; this signal is assigned to hydrogen nuclei, which undergo a fast exchange between water molecules and hydroxonium ions [17]. The coalescence of the 6.5- and 4-ppm-signals can be explained by the fact that at this temperature, all bridging hydroxyl groups are involved in a fast exchange among bridging hydroxyl groups, water molecules, and hydroxonium ions. The mean residence time for this medium chemical exchange also should be on an order of magnitude of 100 µs at 458 K.

A previous investigation of zeolites H-Y and H-ZSM-5 loaded with 0.33 and 1.0 water molecules p.c. [14] found that the center of gravity of the ^{1}H MAS NMR spectrum shifts to higher ppm values when going from 0.33 to 1.0 molecules p.c. This finding can be explained by an increasing amount of hydroxonium species, in agreement with earlier findings on weakly water-loaded zeolites H-Y [25] and H-ZSM-5 [17]. For 0.33 H_2O p.c., no significant changes were seen for zeolite H-Y [14], whereas drastic changes occurred in the spectra of the water-loaded zeolite H-ZSM-5 compared with the unloaded zeolite (see Fig. 7 and Table 4). For 1.0 H_2O p.c., line broadening and a shift to higher ppm values were seen for zeolite H-Y as well [14]. This indicates that the exchange of water/hydroxonium species with bridging hydroxyls is much stronger for zeolite H-ZSM-5 than for zeolite H-Y, in agreement with the higher acidity of H-ZSM-5 compared with H-Y [26]. The effect also could be seen for the ammonia-loaded zeolites. For H-ZSM-5, the merging of ammonium and hydroxyl signals occurred at temperatures 50 K below that for H-Y [14].

Loading with small amounts of water or ammonia molecules creates proton vehicles, which increase the mobility of bridging hydroxyl groups. It is evident from the ammonium signal in the ^{1}H MAS NMR spectra that in the case of ammonia loading, the vehicle is an ammonium ion. The spectra also provide strong evidence that in the case of water loading, the vehicle is a hydroxonium species. Isolated water molecules exhibit a chemical shift of 0.31 ppm [27]. Fully hydrogen-bonded water molecules in bulk water have a well-known shift of 4.78 ppm. Shifts of hydroxonium species are in the range of 7–19 ppm [17]. A hydroxonium cluster comprising three water molecules and one hydroxonium ion should have an average shift of 8.3 ppm [14]. Thus, the observed shift to higher ppm values on weak water loading can be explained only by hydroxonium species. Comparing the influence of small, comparable amounts of water or ammonia loadings shows that the influence of water on line broadening occurs at ca. 10 degrees lower than that of ammonia, indicating that water molecules provide a better proton vehicle.

Finally, we return to the discussion of the proton mobility in zeolites activated at temperatures of 573–723 K. The concentration of residual water molecules or ammonium ions is very small. For H-ZSM-5, the number of residual ammonium ions per crossing is 0.3 at an activation temperature of 570 K, 0.13

at 590 K, and 0.08 at 610 K. Thus, in this temperature range, the number residual ammonium ions is halved with a 20-K increase in activation temperature. Our accuracy of measurement allows us to state that zeolite H-Y activated at 573 K and zeolite H-ZSM-5 activated at 636 K have less than 1 ammonium ion per 30 cavities or crossings.

For zeolite H-Y at an activation temperature of 573 K, the laser experiments detected the onset of narrowing at 532 K with a correlation time of 73 µs. The latter should correspond to the mean residence time, τ_{OH}, between two jumps of bridging hydroxyl groups. This parameter can be determined at lower temperatures on reammoniated samples. The parameter τ_{ammonium} was found to be independent of the loading, and for τ_{OH} we have $\tau_{\mathrm{OH}} = \tau_{\mathrm{ammonium}} \times n_{\mathrm{OH}}/n_{\mathrm{ammonium}}$ with n_{ammonium} and n_{OH} as concentrations of hydrogen atoms in ammonium ions and hydroxyl groups, respectively. With four hydroxyls on O1 positions and fewer than 1/30 ammonium ions (4/30 hydrogen nuclei), we obtain $n_{\mathrm{OH}}/n_{\mathrm{ammonium}} > 30$. We neglect the difference between 532 and 540 K and remember the value $\tau_{\mathrm{ammonium}} = 0.2$–$2$ ms for 540 K. Finally, we obtain $\tau_{\mathrm{OH}} >$ 6–60 ms. But the parameter τ_{OH} from the correlation time of the laser experiment is 73 µs. We can conclude that proton mobility in zeolites H-Y activated at 573 K and above is not influenced by residual ammonium ions.

For zeolite H-ZSM-5 with an activation temperature of 573 K, the situation is different. The laser experiments demonstrated 88 µs at 515 K; τ_{ammonium} could not be measured for H-ZSM-5. We can assume that the mobility is dominated by the influence of residual ammonium ions, and that the aforementioned value of 88 µs is equal to τ_{OH}. Then we take the measured values of 0.3 residual ammonium ions p.c. and 1.7 bridging hydroxyls p.c., from which we obtain the value $\tau_{\mathrm{ammonium}} = 62$ µs for 515 K. Thus is much shorter than the extrapolated value for zeolite H-Y. But from the line broadenings, we conclude that the ammonium-induced mobility is stronger for H-ZSM-5 than for H-Y, therefore, τ_{ammonium} can be short. Another finding hints at an effect of the residual ions at this activation temperature; Table 7 gives the energies obtained from the slopes in the Arrhenius plots depending on the activation temperature. At 573 K, the value of 40.9 $\mathrm{kJ\,mol^{-1}}$ lies within the range of 50 ± 10 $\mathrm{kJ\,mol^{-1}}$ obtained for hydrogen exchange between ammonium ions and bridging hydroxyl groups in reammoniated zeolite H-Y. Therefore, the proton mobility in zeolite H-ZSM-5 activated at 573 K can be influenced by residual ammonium ions. Note that our activation energy agrees with that of 49–59 $\mathrm{kJ\,mol^{-1}}$ reported by Franke and Simon [8] for ammonia-loaded zeolites. At higher activation temperatures, the residual ammonium concentration is drastically reduced, with a decrease in apparent activation energy from 40.9 to 17.3 $\mathrm{kJ\,mol^{-1}}$ (see Table 7). The mechanism of proton mobility seems to change as well.

We argue that hydroxonium species are better proton vehicles than the ammonium ion; however, we cannot determine the concentration of residual water molecules or obtain dynamic parameters connected with this mechanism. It is generally impossible to determine the concentration of a small amount of water molecules in hydrogen zeolites. Heating the zeolite to higher temperature leads to dehydroxylation and dealumination. We obtain water molecules, which can be seen in thermogravimetric studies. Dehydroxylation depends on temperature and water vapor pressure in the zeolite bed; therefore, thermogravimetric analysis cannot characterize the situation in our fused glass ampules. Nonetheless, our findings provide a strong argument against the influence of residual water molecules on proton mobility in zeolites activated at temperatures $\geqslant$573 K (H-Y) or $\geqslant$673 K (H-ZSM-5). Although a significant decrease in residual water molecules would be expected with increasing activation temperature in this wide range, our temperature-dependent ^{1}H MAS NMR spectra show no corresponding differences. In conclusion, we see no hint of the influence of hydroxonium species as proton vehicles for hydrogen zeolites activated at 573–723 K.

A proton vehicle mechanism has not been included in theoretical considerations of proton mobility [28]. *Ab inito* predictions of the proton-transfer reaction rates between neighboring oxygen atoms of an $\mathrm{AlO_4}$ tetrahedron in hydrogen forms of faujasite and ZSM-5 zeolites yielded jump rates over a broad range of 10^{-6} to 10^{5} $\mathrm{s^{-1}}$ at room temperature, depending on the zeolite type and the particular proton jump path within a given zeolite [29]. The final proton jump barriers were between 68 and 106 $\mathrm{kJ\,mol^{-1}}$ for H-Y and between 52 and 98 $\mathrm{kJ\,mol^{-1}}$ for H-ZSM-5; these data correspond to one-site jumps [29]. Multiple-site jumps in H-ZSM-5 at 298–673 K for H-ZSM-5 with one aluminum per unit cell varied over a wider range, 10^{-10} to 10^{10} $\mathrm{s^{-1}}$ [28]. Our zeolite H-ZSM-5 had about 7.3 aluminum atoms per unit cell; nevertheless, we can use some results from DFT calculations [28] in our discussion. Franke et al. [28] claimed that "the energy required to "deprotonate" the $(\mathrm{AlO_4})$H site is largely compensated for by the energy gained by adding the proton to a Si–O–Si bridge. This makes translational intersite hopping of protons possible in zeolites [28]. This mechanism facilitates a multiple-site jump between distant SiOHAl sites. Concerning the apparent activation energy, we can use the result that the activation barrier for the initial jump of the proton away from the $\mathrm{AlO_4}$ site decreases from 127 to 83 $\mathrm{kJ\,mol^{-1}}$ when the spatial separation of two neighboring aluminum sites decreases from 1.4 to 0.6 nm" [28]. With 7.3 aluminum atoms per unit cell, we have spatial separations of about 0.7 nm, but our apparent activation energy (medium value for 673 and 723 K activation temperature) is about 20 $\mathrm{kJ\,mol^{-1}}$. The value increases when going from H-ZSM-5 to H-Y (see Table 7), whereas the spatial separation of aluminum atoms decreases.

The observed proton mobility also can be explained by a homolytic decomposition of the Brønsted sites [30], which yields hydrogen gas molecules and $(\mathrm{AlO_4})^0$ sites.

5. Conclusion

The important hydrogen zeolites H-Y and H-ZSM-5 were investigated by ^{1}H MAS NMR spectroscopy a wide temperature range of 160–773 K to study the proton mobility of Brønsted sites, an elementary problem in catalysis. Signal narrowing by up to a factor of 40 could be assigned to different hydrogen exchange reactions in the zeolites, which were activated in the temperature range of 573–723 K.

We found that the hydrogen form of a zeolite is an ammonium-conducting material if it contains a small amount of ammonium ions ($\geqslant 0.1$ ions per cage or crossing, p.c.). The mean residence time of the hydrogen atoms in the ammonium ions (before exchanging with bridging hydroxyl groups) is independent of the concentration of ammonium ions and has an apparent activation energy of $50 \pm 10\ \text{kJ mol}^{-1}$.

Proton vehicles can be created by weak rehydration (0.33 and 1.0 water molecules p.c.). For the zeolite H-ZSM-5 activated at 673 K and loaded with 0.33 H_2O, the signal of bridging hydroxyl groups disappeared at 340 K due to a decrease in residence time by an order of magnitude of 100 μs. For the unloaded zeolite, such a short residence time was achieved only by increasing the measuring temperature to 481 K.

The dynamic data obtained by temperature-dependent ^{1}H MAS NMR spectroscopy demonstrate multiple-site jumps between different aluminum sites. One-site jumps of the proton over the four oxygen positions around one aluminum site are too fast for observation by NMR.

The greater mobility of the bridging hydroxyl protons seen in zeolite H-ZSM-5 compared with H-Y is consistent with the greater acidity of H-ZSM-5 [26]. We conclude that a proton vehicle mechanism cannot be responsible for this finding, because mobility is not significantly dependent on activation temperature in the given range. It can be explained by intersite hopping of protons between aluminum sites (≡SiOHAl≡) via Si–O–Si bridges [28]; apparent activation energies of this hopping were 53.5–76.6 kJ mol^{-1} for H-Y and 17.3–23.0 kJ mol^{-1} for H-ZSM-5. Another explanation is proton mobility via hydrogen gas molecules created by a homolytic decomposition of the Brønsted sites.

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