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Proton Transfer between Brønsted Sites and Benzene Molecules in Zeolites H-Y Studied by *in situ* MAS NMR

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***In situ* ^{1}H MAS NMR spectroscopy of the proton transfer between bridging hydroxyl groups and benzene molecules yields temperature-dependent exchange rates over more than five orders of magnitude. H-D exchange and NOESY MAS NMR experiments were performed by conventional and laser heating up to 600 K. It is shown that the dealumination of the zeolite has a strong influence on this exchange rate, which represents a dynamic measure of Brønsted acidity.** © 1998 Academic Press

Key Words: In situ **^{1}H MAS NMR; zeolite HY; benzene; acidity; proton transfer.**

INTRODUCTION

Bridging hydroxyl groups capable of donating protons to molecules in the cages of zeolites are Brønsted-acid sites in heterogeneous catalysis (1). It has been demonstrated in the past that the determination of the probability of the proton transfer represents a dynamic measure of the Brønsted acidity (2). Several groups have recently shown that the application of new MAS (magic-angle spinning) techniques facilitates *in situ* NMR studies of catalytic reactions in zeolites (3–5).

The proton transfer between bridging hydroxyl groups (2, 6, 7) or acid sites in sulfated zirconias (8) and benzene molecules has been investigated as an example for a first elementary step of a catalytic reaction also by NMR. The H-D exchange of deuterated benzene in zeolite H-ZSM-5 could be observed even at room temperature (6, 7). Beck *et al.* (9) found in temperature range up to 393 K for the benzene exchange reaction in the zeolites H-ZSM-5, USY and H,Na-Y activation energies of 60, 85, and 107 kJ mol^{-1}, respectively, and carried out quantum chemical calculations of the proton transfer (9, 10).

The catalytic activity of a zeolite is strongly affected by a mild steaming of the hydrogen form (cf. Ref. (11)). This pretreatment does not change the crystalline structure of the zeolite, but it causes a weak dealuminination of the framework and creates nonframework aluminum species (12), which are visible in the ^{1}H and ^{27}Al NMR spectra of the hydrated and dehydrated samples as well (13). The ^{1}H MAS chemical shift of bridging hydroxyl groups is commonly a measure of acidity (1), but it does not indicate an enhanced acidity of bridging hydroxyl groups in weakly dealuminated and dehydrated hydrogen zeolites (12). Therefore, in the present work we determine the proton exchange rate between bridging hydroxyl groups and adsorbed molecules of benzene by *in situ* MAS NMR experiments in a wide temperature range that is limited by a conversion of the benzene molecules in the zeolite above 600 K. This dynamic measure reflects the proton donator properties of the zeolite in accordance to the classic definition by J. N. Brønsted: "that an acid is defined as a substance, which is able to split off H$^+$-ions simultaneously forming a base..." (14). The variation of exchange rates over more than five orders of magnitude that depends on temperature and sample pretreatment provides information about activation energies of the proton transfer and about the preexponential factor of the Arrhenius plot $k = k_0 \exp\{-E_A/RT\}$. The dealumination increases the Si/Al ratio of the framework, which influences the deprotonation energy (cf. (15)), and nonframework aluminum species can give rise to a confinement effect, which influences the activation of molecules in the zeolite cage (16). Sauer and co-worker claimed that a correlation between ^{1}H NMR chemical shifts and heats of deprotonation can be found (17) and cannot be found (15). Their recent negative statement (15) has been derived from a comparison between the four proton positions in faujasite. However, the finding that the ^{1}H MAS chemical shift of bridging hydroxyl groups is a measure of acidity (1) has been limited to the most important position in faujasites, which is denoted as O1. The main problem for the relationship between the ^{1}H MAS chemical shift of bridging hydroxyl groups in zeolites and their acidity is less the theoretical background but more the relatively large linewidth (ca 1 ppm) of the ^{1}H MAS NMR signals compared to the range of their differences in the chemical shift (ca 1 ppm).

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Three MAS NMR techniques were applied in the present study: First, conventional heating of the MAS bearing gas is used up to 520 K for H-D exchange reaction rates up to about 0.1 per minute. Second, the temperature jump method by means of laser heating (18) could be used for monitoring H-D exchange reaction rates up to about 10 min^{-1}. Third, we present for the first time a two-dimensional ^{1}H NOESY MAS NMR exchange spectrum, which has been measured at 520 K, and we obtained exchange rates in the order of magnitude of 100 min^{-1} for the H-H exchange at temperatures up to 600 K.

EXPERIMENTAL

The zeolite 92 H-Y (Si/Al = 3.1) containing 8% of the original content of Na^+ cations and some nonframework aluminum species was prepared by Dr. J. Meusinger by a repeated exchange of zeolite Na-Y in an aqueous solution of NH_4NO_3 followed by calcination. The defect-free zeolite 85 H-Y (85% NH_4^+ and 15% Na^+, Si/Al = 2.4) was donated by UOP. The third sample is a partially dealuminated zeolite (Si/Al = 2.8), which was obtained from the parent zeolite 85 H-Y by the following procedure: The zeolite layer of 2 g was pretreated in a bed with 5 mm maximum bed-depth. Temperature was increased at a rate of 10 K h^{-1} in a water free nitrogen stream. Steaming was carried out at 673 K for 90 min under water vapor pressure of 15 kPa. The framework Si/Al ratios have been determined by ^{29}Si MAS NMR.

Samples were pretreated by heating 8 mm deep layers of zeolite in glass tubes 5 mm outer diameter at a rate of 10 K h^{-1} under vacuum. After maintaining the samples at 673 K and less than 10^{-2} Pa for 24 h, they were loaded under vacuum at room temperature with two molecules benzene per supercage (1/8 unit cell) and then sealed. Benzene has been 99.5% enriched in ^{2}H for the H-D exchange experiments. The samples were kept frozen until the start of the NMR measurement.

The *in situ* ^{1}H MAS NMR spectra of the sealed samples were recorded at 300 MHz and spinning rates of 2–4 kHz. The duration of a $\pi/2$ pulse has been ca 5 μs, the ring-down delay was 25 μs and the signals were acquired in a distance of about 8 s. The calibration of the temperature in the probes (Bruker high-temperature MAS probe and 50 W CO_2 laser MAS probe) was carried out with lead nitrate as ^{207}Pb NMR thermometer (19–21). The one-dimensional H-D exchange experiment in the high-temperature MAS probe has been performed as follows: After preheating the probe to the desired temperature for some minutes, the sample was inserted into the probe, and the heating was continued. The acquisition of the first spectrum was started as soon as the thermocouple (placed in the MAS stator) indicates the desired temperature again. The temperature gradient in the glass sample has been determined (cf. (18)), to ±10 K at 520 K and ±2 K at 350 K. The laser probe and the temperature jump technique were described in Refs. (18, 22). The temperature gradient in the laser probe has been ±33 K at 600 K. Two-dimensional MAS NMR exchange experiments were performed by means of a $\pi/2$-t_1-$\pi/2$-t_m-$\pi/2$-t_2 pulse sequence, where t_1, t_m, and t_2 denote the evolution time, mixing period and acquisition time, respectively (cf. (23)). This pulse program is commonly denoted as NOESY. Cross peaks appear in the obtained 2D spectrum, if a chemical exchange of the protons between the molecules and bridging hydroxyl groups takes place. Room temperature ^{1}H MAS NMR measurements of C_6H_6 loaded samples do not show a variation of the signal before and after heating at 600 K. Thus, benzene molecules were not converted at temperatures up to 600 K. But the benzene signal disappears after heating at 650 K.

RESULTS AND DISCUSSION

^{1}H, ^{27}Al, and ^{29}Si MAS NMR spectra of the dehydrated (^{1}H) and hydrated (^{27}Al and ^{29}Si) zeolites HY were already published (13). There is a very small change (0.1 ppm low field) of the chemical shift of bridging hydroxyls upon dealumination, although in the case of 92 H-Y the dealumination is monitored by other signals in the spectra.

Figure 1 gives the results of a H-D exchange experiment at 400 K. A certain exchange takes place in the time, when the sample is heated up from room temperature to the desired temperature in the probe. Therefore, the

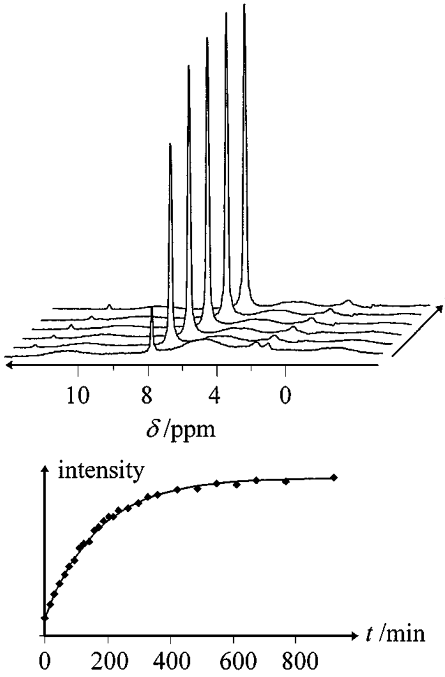


FIG. 1. Time dependence of the ^{1}H MAS NMR spectra of the zeolite 85 H-Y loaded with fully deuterated benzene. The spectra were measured at 400 K. Integrated intensities of the benzene signal at 7.5 ppm and a fit according to Eq. [1] are given.

concentration of ^{1}H nuclei in benzene is already above zero for the first measured spectrum. The time dependent ^{1}H NMR intensity can be described by

$$I(t) = I(\infty)(1 - b\exp(-kt)), \qquad [1]$$

where k is the exchange rate and $I(\infty)$ denotes the intensity after a full exchange. The value b describes the exchange at $t = 0$. The maximum value of k, which was obtained with a sufficient accuracy in a H-D exchange experiment by means of conventional heating is $k = (9.4 \pm 0.9) \times 10^{-2}$ min^{-1} with $b = 0.5$ for 440 K. The accuracy increases for lower values of the exchange rate, e.g., $k = (2 \pm 0.1) \times 10^{-3}$ min^{-1} at 350 K.

The initial state ($t = 0$) of the H-D exchange experiment is characterized by fully deuterated molecules and nondeuterated bridging hydroxyl groups. For the value $n_{\mathrm{B}} = n_{\mathrm{B}}^{\mathrm{H}} + n_{\mathrm{B}}^{\mathrm{D}}$, which denotes the number of the hydrogen positions in the benzene molecules per cavity (1/8 unit cell), it holds $n_{\mathrm{B}} = n_{\mathrm{B}}^{\mathrm{D}}(0)$. The number of bridging hydroxyl groups per unit cell which take part in the exchange is denoted as $n_{\mathrm{A}} = n_{\mathrm{A}}^{\mathrm{H}} + n_{\mathrm{A}}^{\mathrm{D}}$ and it holds $n_{\mathrm{A}} = n_{\mathrm{A}}^{\mathrm{H}}(0)$. The equilibrium numbers after the exchange $n_{\mathrm{A}}^{\mathrm{H}}(\infty)$ and $n_{\mathrm{B}}^{\mathrm{H}}(\infty)$ or their ratio are

$$n_{\mathrm{A}}^{\mathrm{H}}(\infty) = \frac{n_{\mathrm{A}}^2}{n_{\mathrm{A}} + n_{\mathrm{B}}} \quad \text{and} \quad n_{\mathrm{B}}^{\mathrm{H}}(\infty) = \frac{n_{\mathrm{A}} n_{\mathrm{B}}}{n_{\mathrm{A}} + n_{\mathrm{B}}},$$

$$\text{or} \quad \frac{n_{\mathrm{A}}^{\mathrm{H}}(\infty)}{n_{\mathrm{B}}^{\mathrm{H}}(\infty)} = \frac{n_{\mathrm{A}}}{n_{\mathrm{B}}} = \frac{\tau_{\mathrm{A}}}{\tau_{\mathrm{B}}}, \qquad [2]$$

respectively, where τ_{A} and τ_{B} denote the mean life times of the protons in the bridging hydroxyl groups and benzene molecules, respectively (2). The measured reaction rate k is described by

$$k = \left(\frac{1}{\tau_{\mathrm{A}}} + \frac{1}{\tau_{\mathrm{B}}}\right) = \frac{1}{\tau_{\mathrm{A}}}\left(1 + \frac{n_{\mathrm{A}}}{n_{\mathrm{B}}}\right) = \frac{1}{\tau_{\mathrm{A}} n_{\mathrm{B}}}(n_{\mathrm{A}} + n_{\mathrm{B}}). \qquad [3]$$

It should be noted that exchange rates can be easily recalculated, if a second-order reaction is considered. Our study is related to one zeolite structure (H-Y) and one loading. The given number of bridging hydroxyl groups (six per cavity for 85 H-Y or 5.4 for 92 H-Y (cf. (13)) and the given loading (two benzene molecules per cavity) obtains $n_{\mathrm{A}} + n_{\mathrm{B}} = 18$, or 17.6 per cavity, respectively. A narrow signal of desorbed benzene molecules in the gas phase at 7.27 ppm could not be observed, even at the maximum temperature of measurement. Therefore, $n_{\mathrm{A}} + n_{\mathrm{B}}$ is a temperature-independent value. The temperature-dependent changes of the reaction rate k are caused by the changes of the mean residence time τ_{A} of a hydroxyl proton before the transfer to the base molecule. Thus, the experimentally obtained reaction rate k represents a dynamic measure of Brønsted acidity.

With increasing temperatures the reciprocal exchange rate becomes as short as the longitudinal relaxation time. Then the exchange reaction can be monitored by ^{1}H NOESY MAS NMR (23). The cross peaks in the spectrum obtained at 520 K (cf. Fig. 2) demonstrate the magnetization transfer between the relatively broad signal of the bridging hydroxyl groups at ca 4 ppm and the benzene signal at ca 7.5 ppm. The signal at ca 2 ppm due to nonacidic hydroxyl groups on framework defects (13) is not influenced by a magnetization transfer; i.e., only the diagonal peak appears. Figure 3 shows the ^{1}H MAS NMR spectra of benzene adsorbed on zeolite 92 H-Y in dependence of the duration

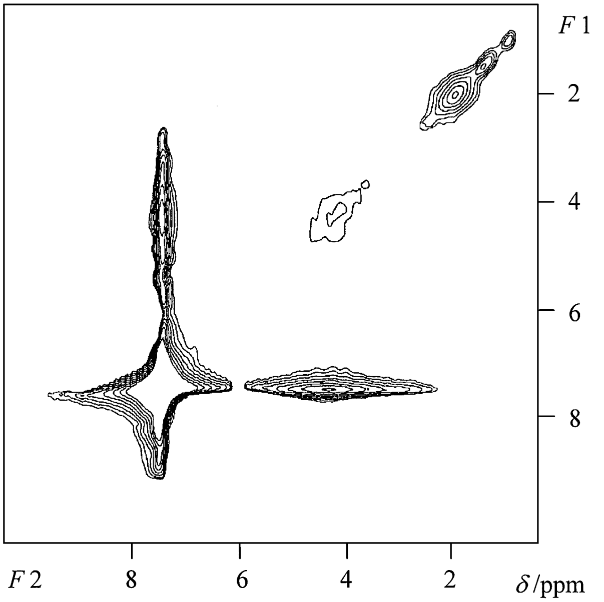


FIG. 2. Two-dimensional ^{1}H NOESY MAS NMR spectrum measured at 520 K with a MAS frequency of 4 kHz and a mixing period of 500 ms. Two benzene molecules per cavity were adsorbed on zeolite 92 H-Y.

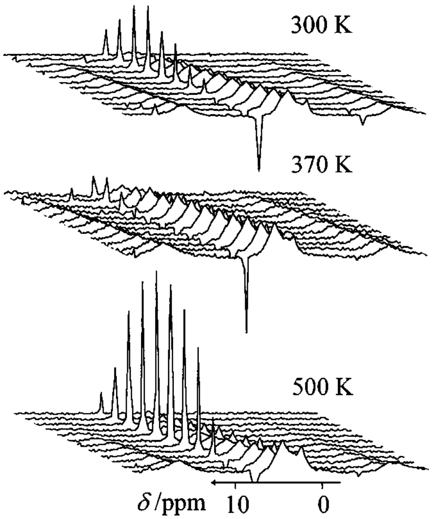


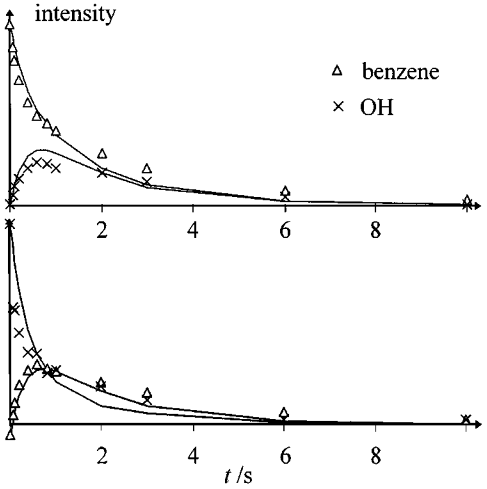
FIG. 3. ^{1}H MAS NMR spectra of benzene adsorbed on zeolite 92 H-Y measured with a NOESY pulse sequence in dependence on the duration of the mixing period from 4 μs, 50 ms, 0.1 s, 0.2 s, . . ., 10 s.

of the mixing period. The frequency offset and the duration of the evolution period t_1 were adjusted to a maximum signal intensity of the bridging OH groups and to a minimum signal intensity of the benzene in the signal for $t_m = 4\ \mu s$ and kept constant for all values of t_m. A zero intensity at the benzene position cannot be achieved, since the narrow benzene signal is much stronger than the broad hydroxyl signal. The magnetization transfer is characterized in Fig. 3 by the relatively narrow benzene signal, which first increases and then decreases, if the mixing period is much longer than the longitudinal relaxation time. At room temperature the magnetization transfer is due to cross relaxation from the OH groups. At the temperature of 370 K only a very small amount of magnetization is transferred by the analogous experiment. This can be explained by an increased mobility, which causes an averaging of the dipolar coupling, which is responsible for the cross relaxation process. However, there is a drastic increase of the magnetization transfer at 500 K (cf. Fig. 3 bottom). This is a strong hint that at higher temperatures pure chemical exchange between the benzene molecules and the OH groups occurs and cross relaxation effects can be neglected. Thus, the cross peaks in the spectrum obtained at 520 K (cf. Fig. 2) are due to the chemical exchange, and exchange rates can be determined from the dependencies on the mixing time t_m.

Without cross relaxation, the dynamic matrix $\boldsymbol{L}$ of magnetization propagation has the form

$$\boldsymbol{L} = -\boldsymbol{R} + \boldsymbol{K} = -\begin{pmatrix} 1/T_{1B} & 0 \\ 0 & 1/T_{1A} \end{pmatrix} + \begin{pmatrix} -1/\tau_B & 1/\tau_A \\ 1/\tau_B & -1/\tau_A \end{pmatrix}, \qquad [4]$$

where $\boldsymbol{R}$ and $\boldsymbol{K}$ denote the relaxation matrix and the kinetic matrix, respectively, which exactly describe the complete time dependence of the intensities for two exchanging sites (23). Two dependencies on the mixing time were measured at each temperature, in order to determine the dynamic matrix $\boldsymbol{L}$. Offset and evolution period were adjusted to values, which in the first set give rise to a minimum or maximum (and in the second set to a maximum or minimum) of the signal intensity at $t_m = 0$ of the OH groups or benzene molecules, respectively. Three independent parameters remain for the fit of the resulting four time-dependent intensities: the longitudinal relaxation times for both species and either τ_A or τ_B. The latter values are connected by Eq. [2] with the ratio n_A/n_B, which can be measured independently. Figure 4 shows the time-dependent intensities of the OH groups and the benzene molecules at 520 K with the fit and the obtained dynamic matrix $\boldsymbol{L}$.



$$\boldsymbol{L} / \mathrm{s}^{-1} = -\begin{pmatrix} 0.53 & 0 \\ 0 & 0.76 \end{pmatrix} + \begin{pmatrix} -0.79 & 1.25 \\ 0.79 & -1.25 \end{pmatrix}$$

FIG. 4. ^{1}H MAS NMR intensities of the benzene molecules and the bridging hydroxyl groups of zeolite 92 H-Y at 520 K. The spectra were measured by a NOESY pulse sequence in dependence on the duration of the mixing period. The dynamic matrix, which is used for the fit of the data, is given below.

The results of the H-H exchange experiments can be combined to those of the H-D exchange experiments (cf. Eqs. (3) and (4)). Figure 5 shows the Arrhenius plot $k = k_0 \exp\{-E_A/RT\}$ for the benzene exchange reaction in the zeolites 85 H-Y and 92 H-Y. The values with $k > 10\ \mathrm{min}^{-1}$ were determined by means of two-dimensional NOESY MAS NMR, whereas other values were obtained by time-resolved H-D exchange experiments. The best fit is given by the solid lines in Fig. 5. The activation energies E_A were obtained as $102 \pm 5\ \mathrm{kJ\ mol}^{-1}$ and $100 \pm 7\ \mathrm{kJ\ mol}^{-1}$ for the zeolites 85 H-Y and 92 H-Y, respectively.

It is well-known that the gas-phase acidity of bridging hydroxyl groups increases if the aluminum content in the framework decreases (1). Zeolite 85 H-Y has a Si/Al ratio of 2.4, for the mildly steamed zeolite 85 H-Y is Si/Al = 2.8

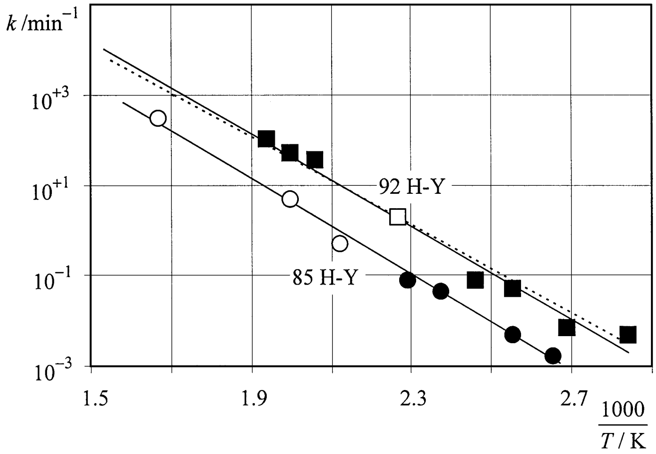


FIG. 5. Arrhenius plot of the H-D and H-H exchange rates for benzene molecules in the zeolites 85 H-Y and 92 H-Y. The values which are marked by open or full circles and squares were measured by laser heating or conventional heating, respectively.

and for the zeolite 92 H-Y is Si/Al = 3.1. The variation of the ^{1}H NMR shift of the bare bridging hydroxyl groups is only 0.1 ppm for the dehydrated zeolites under study. The rates of the proton transfer between bridging hydroxyl groups and benzene molecule are increased by a factor of 3 or 10 going from zeolite 85 H-Y to the mildly steamed 85 H-Y or to 92 H-Y, respectively. This holds for the temperature range 363 K $\leq T \leq$ 408 K, in which the values for the mildly steamed zeolite 85 H-Y were determined. Their exchange rates k, which are not presented in Fig. 5, are increased by a factor of 2 with respect to the values of the nonsteamed zeolite. Thus, the proton transfer rate clearly describes the change of acidity, which is due to Brønsted's definition caused by the proton donator property, whereas the change of the gas phase acidity of the bridging hydroxyl groups has only a weak influence on their ^{1}H NMR chemical shift.

The dotted line for zeolite 92 H-Y is also within the limit of the experimental error and corresponds to a value of 93 kJ mol^{-1}. The extrapolation of the lines to $T = \infty$ gives the preexponential factor k_0 of the Arrhenius plot. A difference of about one order of magnitude is obtained, if the solid lines are used for the determination of the preexponential factors of both zeolites. But only one value of 3×10^9 s^{-1} is obtained for both zeolites, if the dotted line is used instead of the solid line for the zeolite 92 H-Y. Therefore, the experimental data do not allow us to conclude whether the activation energy or the preexponential factor gives rise to the factor of about 10 between the rates for the two zeolites. Beck *et al.* (9) found activation energies for the benzene exchange reaction of 107 kJ mol^{-1} and 85 kJ mol^{-1} in a zeolite HY, which is similar to our zeolite 85 H-Y, and zeolite USY, respectively. The exchange rate at 370 K is higher by more than one order of magnitude for the ultra-stable zeolite USY, which has a Si/Al ratio of 5.4 and contains nonframework aluminum species. This result is similar to our measurement, but the small temperature range in Ref. (9) does not allow an extrapolation to $T = \infty$.

The preexponential factor k_0 is the reaction rate for infinite temperature or zero activation energy and can be discussed in terms of partition functions of the adsorbate complex for the H-D exchange in zeolites, as shown by Kramer and van Santen (24). It is remarkable that the preexponential factor of 3×10^9 s^{-1} is nearly equal to the rotational constant 2.8×10^9 s^{-1} for the benzene rotation (about the C_6 axis) (26), whereas the stretching vibration of the bridging hydroxyl groups is in the order of magnitude of 10^{14} Hz. This is a hint that the rotation of the molecule may play a role for the proton transfer.

Ab initio quantum chemical calculations (17) yield a linear correlation between the ^{1}H NMR shift δ of surface hydroxyl groups or the change of this shift by adsorbed molecules (25) and their deprotonation energy with a slope of (-84 ± 12) kJ mol^{-1} ppm^{-1}. The difference of the ^{1}H NMR shifts between the two zeolites H-Y under study of 0.1 ppm is related to a difference of their deprotonation energies of 8.4 kJ mol^{-1}. This agrees with the difference of the activation energies, which were obtained under the assumption of a constant value of k_0: 102 kJ mol^{-1} for 85 H-Y (solid line in Fig. 5) and 93 kJ mol^{-1} for 92 H-Y (dotted line in Fig. 5). Thus, the variation of the Si/Al ratio, which causes a change of the deprotonation energy, can explain the differences of the exchange rate of one order of magnitude in the temperature region of 350–600 K.

However, a variation of the preexponential factor can be caused by steric effects like the existence of nonframework aluminum species. This would also explain our experimental results.

CONCLUSIONS

The proton transfer in benzene-loaded zeolites HY is studied as an example for the first elementary step of heterogeneous acid catalysis by *in situ* ^{1}H MAS NMR spectroscopy. H-D exchange and NOESY NMR experiments were performed by conventional and laser heating up to 600 K and yield a change of the exchange rate over more than 5 orders of magnitude. A 2D ^{1}H NOESY MAS NMR spectrum, which has been measured at 520 K, shows the chemical exchange between benzene molecules and bridging hydroxyl groups. Silanol groups were not affected.

The rates of the proton transfer between bridging hydroxyl groups and benzene molecules in the temperature region of 350–600 K increase by a factor of 3 or 10, going from zeolite 85 H-Y (Si/Al = 2.4) to the mildly steamed 85 H-Y (Si/Al = 2.8), or to 92 H-Y (Si/Al = 3.1), respectively. The weak dealumination, which causes only a small change of the chemical shift of the bridging hydroxyl groups of 0.1 ppm, has a strong influence on the dynamic measure of Brønsted acidity, which is given by the rate of the proton transfer.

Activation energies of the proton transfer have been obtained under the assumption of a constant value of the preexponential factor in the Arrhenius plot to 102 kJ mol^{-1} for zeolite 85 H-Y (Si/Al = 2.4) and 93 kJ mol^{-1} for zeolite 92 H-Y (Si/Al = 3.1). In this case, the variation of the Si/Al ratio, which causes a change of the deprotonation energy of the bridging hydroxyl groups, can explain the differences of the exchange rate. But a variation of the preexponential factor by steric effects like the existence of nonframework aluminum species cannot be excluded.

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