

FTIR spectroscopic and ^1H MAS NMR studies of the influence of lattice chemistry and structure on Brønsted acidity in zeolites

J. Jänchen¹, J.H.M.C. van Wolput, L.J.M. van de Ven, J.W. de Haan and R.A. van Santen

Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

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The influence of the Si/Al ratio, of the nature of the T-atom and of the pore size on the acidic strength of Brønsted sites in zeolites has been investigated using changes of the vibrational properties of Brønsted OH(OD) groups and a shift change of Brønsted protons in nuclear magnetic resonance upon adsorption of weak bases. Deuterated acetonitrile and trichloro-acetonitrile have been chosen to probe the acidic strengths of ZSM-5, FeZSM-5, mordenite and zeolite Y, which are often used as catalysts. From the results of the FTIR and ^1H MAS NMR studies it can be concluded that the chemical composition of the lattice dominates the acidic strength of the Brønsted sites in zeolites. Differences in structure or pore size play a much smaller role.

Keywords: Brønsted acidity; FTIR; ^1H MAS NMR; adsorption; zeolites

1. Introduction

The influence of zeolite composition, structure type and location of the acidic protons on the acid strength of the bridging protons in zeolites is of obvious importance to the application of zeolites in acid catalyzed reactions. Significant progress has been made to determine this relationship based on different theoretical approaches and using different physico-chemical methods [1].

Although straightforward relationships between spectroscopic parameters of the bridging hydroxyl groups and acidic strength of the catalyst are sometimes invoked [2] or stated explicitly [3], it is becoming clear now that such simple rules are sometimes deceptive. A general statement concerning the importance of sorbate–catalyst interactions in defining catalytic activity was recently made by Bull et al. [4]. A corresponding conclusion regarding measurement of proton-donating ability of a solid acid catalyst by means of the resulting proton chemical shift change of the sorbate was made earlier by Anderson et al. [5]. In older literature, zeolites were often classified as superacids. A clear statement to rectify this situation was recently published by Haw et al. [6,7]. Also, the importance of comparing a sorbate's response to different zeolites was stressed [6]. Extensions of this approach were quite recently published by Freude [8] and by Brunner et al. [9], who again emphasised the importance of studying catalyst–sorbate interactions. A similar approach was followed by this group in studying the acidity of sulfated zirconia [10]. A useful review article was recently published by Pfeifer [11]. An interesting

alternative to studying zeolite–sorbate interaction consists of following the high-temperature behaviour of bridged hydroxyl groups in zeolites with ^1H NMR [12]. In IR spectroscopy the principle of following the response of hydroxyl groups to their interaction with adsorbed weak bases to determine the acidic strength is already well established by Kazansky [13,14] and applied by other groups [15].

In this paper we focus our attention to the influence of the zeolite composition (Si/Al ratio, isomorphous substitution) and of the structure (pore size) on the acid strength of Brønsted sites using FTIR and ^1H MAS NMR with weak bases as probe molecules. Results of quantum chemical calculations [16] already indicate the conclusion that the strength of the Brønsted sites is especially affected by changes in the chemistry, while the structural factor is only of secondary influence. Following the concept of Barthomeuf (NNN-concept) [17] and Kazansky (adsorption of weak bases) we are looking for a correlation between the “true” acidic strength of the bridged hydroxyl groups [10] and the changes of the OH stretching and the OD bending modes in IR as well as their changing shifts in ^1H MAS NMR upon adsorption of acetonitrile or the less basic chloro-acetonitrile for a set of MFI, MOR and FAU type zeolites.

2. Experimental

IR spectra were measured at room temperature on a Bruker FTIR-spectrometer IFS 113v equipped with a vacuum cell. Self-supporting discs with a thickness of 7.5 mg/cm^2 were used. Activation of the samples was performed at 723 K in high vacuum for 1 h. After cooling

¹ Present address: Adlershofer Umweltschutztechnik- und Forschungsgesellschaft mbH, Rudower Chaussee 5, Haus 2.3, 12484 Berlin, Germany.

down to room temperature the spectrum of the unloaded sample was taken, followed by contacting the sample with d_3 -acetonitrile for 30 min at a pressure of approximately 1 mbar. Then again a spectrum was recorded. After this the loading of the samples was reduced stepwise by lowering the equilibrium pressure to 0.05 mbar and by desorption (15 min) at room temperature. Additional spectra were recorded after desorption for 1 h at 353 and 573 K, respectively. Deuteration of the zeolites was carried out at 673 K with deuterium at a pressure of 100 mbar. The exposure time was three times 10 min. After deuteration the wafer was heated again at 723 K for 1 h to remove traces of water.

The ^1H MAS NMR experiments were performed at room temperature on a Bruker NMR spectrometer MSL 400 with a magnetic field of 9.4 T, the MAS spinning rate was 5–10 kHz. 16 FID's were accumulated by using 90° pulses ($1.5\ \mu\text{s}$) with a repetition time of 5–60 s. The samples for the NMR experiment were also degassed on a vacuum line at 723 K for 3–5 h in high vacuum. After cooling to room temperature adsorption was carried out at equilibrium pressures (1 mbar or 0.01 mbar for CCl_3CN ; 0.5 mbar or 0.01 mbar for CD_3CN , at 297 K). The lower pressure corresponds to about one base molecule per Brønsted site or less (HY). After adsorption, the samples were kept in a sealed tube. Prior to the NMR experiment the samples were transferred into tightly closed rotors (standard 4 mm rotors) in a glove box.

The zeolites used came from different sources. The preparation and characterization of the MFI type samples and of the FAU zeolites are described in ref. [18] and ref. [19], respectively. The mordenite samples were obtained from the Shell company and are modified by hydrothermal treatment to get Si/Al ratios of 6.7 and 10, respectively. The corresponding values are for H-ZSM-5 52, H-Fe-MFI 32 (Si/Fe ratio in the framework), H-Y 5 and 18 as well as NaHY/CsHY 2.4. The Si/Al of ratios of the FAU and the MOR have been chosen between values lower and higher than the critical ratio which gives no next nearest neighbour for Al in the structure (FAU = 5.8, MOR = 9.5). The MFI type zeolites do not have such a value [17]. Therefore, the acidic strength has been varied by isomorphous substitution of Al by Fe.

3. Results and discussion

Fig. 1 shows the changes of the IR spectra in the $1400\text{--}4000\ \text{cm}^{-1}$ region upon adsorption of deuterated acetonitrile on H-ZSM-5, H-MOR and H-Y zeolites with different Si/Al ratios. The bands of the OH stretching vibrations in the region of about $3600\ \text{cm}^{-1}$ disappear and shift downwards upon adsorption of CD_3CN , whereby the extent of this shift depends on the acid strength of the OH. Secondly, the CN stretching mode of the base shifts upwards from $2265\ \text{cm}^{-1}$ (for the free

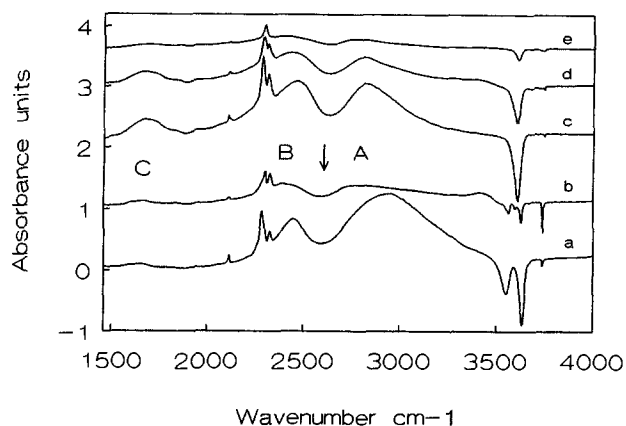


Fig. 1. Difference spectra of CD_3CN adsorbed on H-zeolites with different Si/Al ratios at an equilibrium pressure of 0.05 mbar; (a) H-Y(5); (b) H-Y(18); (c) MOR(6.7); (d) MOR(10); (e) H-ZSM-5(52).

molecule) in a characteristic way due to a Brønsted complex (to about $2300\ \text{cm}^{-1}$) or a Lewis bonded molecule (to $2320\text{--}2330\ \text{cm}^{-1}$) [20].

The "Brønsted bands" shift downwards by $1000\ \text{cm}^{-1}$, typical for strong bridging OH in zeolites. Interestingly, the adsorption of the base on the acidic OH leads to a shifted broad band split into two or three pseudo-bands, the so-called A, B and C branches. This is due to resonant interactions between the OH stretching and overtone bending modes (dip at $2600\ \text{cm}^{-1}$ of the perturbed bridging OH) [20,21]. Thus the frequency of the shifted $\nu(\text{OH})$ has to be estimated by evaluating the centre of gravity of these pseudo-bands. From fig. 1 it can already be seen that the shift and distribution of intensity of these very broad bands are different and depend on the Si/Al ratio of the corresponding zeolite. The highest values are found for the large pore zeolite H-Y(18) and for the small pore zeolite H-ZSM-5 having the highest Si/Al ratio.

A weaker base such as CCl_3CN should cause a smaller shift upon adsorption. This is indeed the case as can be seen in fig. 2. The C bands do not occur, the broad bands are less shifted (by about $600\text{--}700\ \text{cm}^{-1}$) and are less broad. The dip (see arrow) stays at the same position and the intensity of the A band is higher compared with the more basic deuterated acetonitrile. All these facts point to a lower disturbance of the OH stretching modes or a weaker complex OH-base.

Fig. 3 compares the difference spectra of some FAU zeolites recorded after adsorption of 0.05 mbar CD_3CN . Not only the Si/Al ratio but also the kind and amount of cations differ, resulting in samples which contain both the LF and HF bands and those having the HF (NaHY) or the LF band (CsHY) only. In this way it can be demonstrated that the LF band is much weaker than the HF band in apparent contradiction to the frequency of the unloaded Brønsted sites. The reason is the formation of a weak hydrogen bond of the proton in the double six-ring, attached to the $\text{O}_{(3)}$ of the FAU structure, with

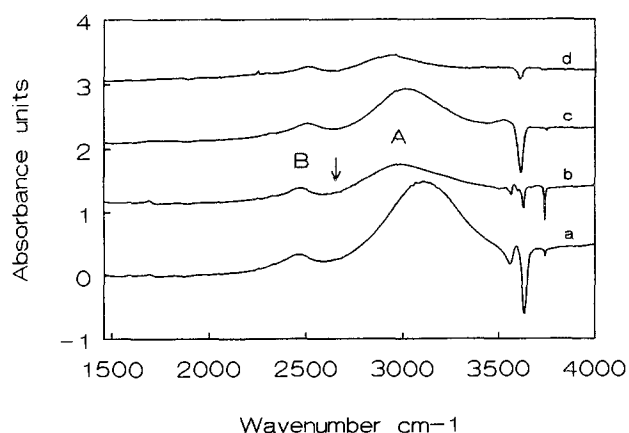


Fig. 2. Difference spectra of CCl_3CN adsorbed on H-zeolites with different Si/Al ratios at an equilibrium pressure of 0.05 mbar; (a) H-Y(5); (b) H-Y(18); (c) MOR(6.7); (d) H-ZSM-5(52).

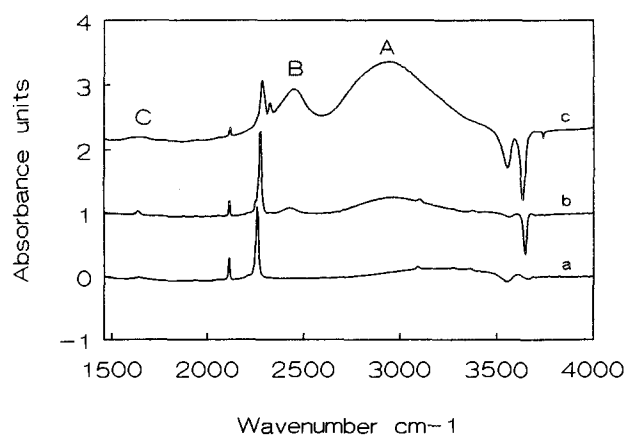


Fig. 3. Difference spectra of CD_3CN adsorbed on FAU zeolites with different Si/Al ratio and extents of cation exchange at equilibrium pressure of 0.05 mbar; (a) CsHY(2.4); (b) NaHY(2.4); (c) HY(5).

another oxygen. This shifts the OH stretching mode of the LF band downwards and disguises the strong acidity. Therefore, the adsorption of a base and the response of the OH is the only proper way to characterize acidity by vibrational spectroscopy.

In table 1 are summarized the results of the FTIR measurements regarding the influence on OH stretching modes of adsorption of CCl_3CN and CD_3CN . Included is the comparison of H-ZSM-5 with its isomorphously substituted form, H-Fe-MFI. The replacement of Al by Fe in the lattice of the MFI structure reduces the shift of the OH stretching upon adsorption of CD_3CN and CCl_3CN by 110 and 80 cm^{-1} , respectively. Again the chemical factor changes the acidic strength of the bridging OH. This was verified by microcalorimetric measurements of ammonia adsorption on both samples [22]. The heat of chemisorption is significantly lower (10 kJ/mol) for Fe-MFI compared to the Al form of the structure.

If the protons of the H-forms of the zeolites are exchanged against deuterium the bending modes become

visible in the window at about 850–950 cm^{-1} between the strong lattice T–O vibrations [23]. Thus the effect of the interaction of bases on the position of the bending modes can be measured directly. Table 2 lists the wavenumbers before adsorption of the two bases and the shifts of the bending modes upon adsorption for different zeolites. As would be expected from the behaviour of the stretching modes, a correlation between the shifts and the chemical factor of the samples is found.

MAS NMR techniques are widely used to characterize acidity of zeolites [24–26]. In analogy to the IR experiments we carried out ^1H MAS NMR measurements not only on unloaded samples but also on zeolites with different adsorbed amounts of the two probes, thus observing the response of the acidic protons as already pointed out above.

For comparison fig. 4 shows the ^1H MAS NMR spectra of H-ZSM-5, H-MOR and H-Y zeolite without adsorption. As can be seen, the signals for the acidic protons appear at a chemical shift of approximately 4–5 ppm. The silanol protons cause a line at 2 ppm. An addi-

Table 1

IR OH stretching wavenumbers, $\nu(\text{OH})$ in cm^{-1} , of different zeolites and their change, $\nu(\text{OH})^a$ and their shift $\Delta\nu$ in cm^{-1} , upon adsorption of CCl_3CN and CD_3CN ; equilibrium pressure 0.05 mbar

Sample	$\nu(\text{OH})$ before adsorption	$\nu(\text{OH})$ after CCl_3CN adsorption	$\Delta\nu$ after CCl_3CN adsorption	$\nu(\text{OH})$ after CD_3CN adsorption	$\Delta\nu$ after CD_3CN adsorption
H-ZSM-5(52)	3610	2890	720	2500	1110
H-Fe-MFI(32)	3630	2990	640	2610	1020
H-Y(18)	3629	2960 ^b	669 ^b	2590 ^b	1039 ^b
	3550				
H-MOR(10)	3609	—	—	2540	1069
H-MOR(6.7)	3610	2960	650	2560	1050
H-Y(5)	3630	3050 ^b	580 ^b	2680 ^b	950 ^b
	3550				
NaHY(2.4)	3647	3150	497	2900	747
CsHY(2.4)	3554	—	—	3130	424

^a Centre of gravity of the A, B and C bands.

^b Complicated because “mixture” of two different OH (LF, HF); at lower adsorbed amount the $\nu(\text{OH})$ values are lower and the $\Delta\nu$ higher.

Table 2

IR OD bending wavenumbers, $\delta(\text{OD})$ in cm^{-1} , of different D/H zeolites and their shifts, $\Delta\delta(\text{OD})$, upon adsorption of CCl_3CN and CD_3CN ; equilibrium pressure 0.05 mbar

Sample	$\delta(\text{OD})$ before adsorption	$\Delta\delta(\text{OD})$ after CCl_3CN adsorption	$\Delta\delta(\text{OD})$ after CD_3CN adsorption
D-ZSM-5(52)	894	+78	+94
D-Fe-MFI(32)	865	+65	+85
D-Y(18)	876 (897) ^a	+75	+92
D-MOR(6.7)	(888) ^b 891	+62	+82
D-Y(5)	872 (890) ^a	+58	+77

^a Shoulder, from the LF OH stretching mode.

^b Shoulder.

tional signal at 2.8 ppm is found for the H-Y zeolites and, less pronounced, for the H-MOR due to OH on extra-framework Al. In agreement with this, AlO–H stretching modes are also present in the IR spectra (figs. 1 and 2). The acidic protons in HY pointing into the large cavities show a signal at 4.1 ppm, the same value as found for protons in H-MOR and HZSM-5, and the less acidic protons in H-Y, pointing into the six-ring, reveal a

shift of 4.7 ppm. This in itself is already a strong indication that chemical shifts in ^1H NMR as such are of limited use in distinguishing acidic strengths in zeolites.

Fig. 5 displays the ^1H MAS NMR spectra of the loaded zeolites as well. Upon adsorption of CD_3CN at 0.01 mbar the signals for the acidic protons at 4 ppm shift to 10.3–11.2 ppm. A small shoulder found for mordenite at about 12.5 ppm (traces c and d), suggests some even stronger sites which cannot yet be assigned. Good agreement was found with results of Haw et al. [6] for ZSM-5 ($\text{Si}/\text{Al} = 20$). Whereas the signals of all acidic protons in the MFI and MOR samples shift at the chosen low equilibrium pressure, the “LF band” of the FAU samples does not shift completely. As can be seen in fig. 6, increase of the equilibrium pressure enhances also the

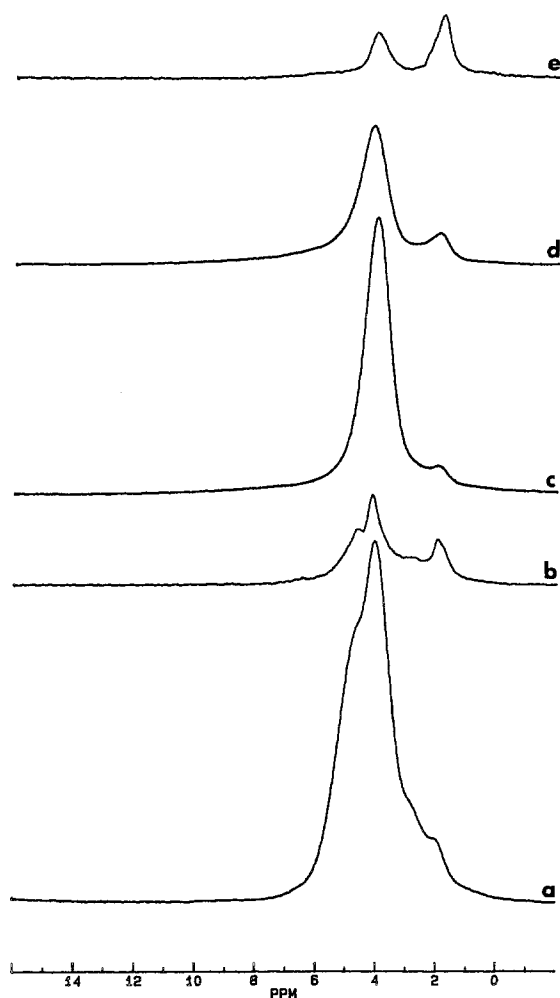


Fig. 4. ^1H MAS NMR spectra of H-zeolites investigated; (a) H-Y(5); (b) H-Y(18); (c) MOR(6.7); (d) MOR(10); (e) H-ZSM-5(52).

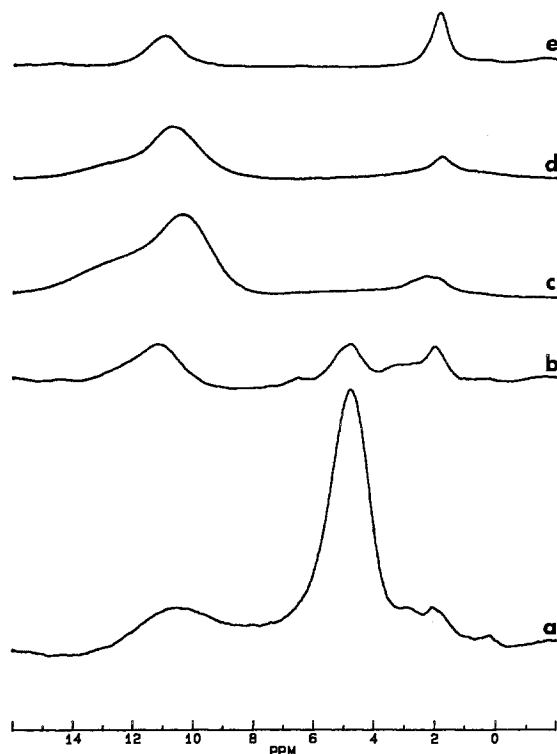


Fig. 5. ^1H MAS NMR spectra of H-zeolites upon adsorption of CD_3CN at an equilibrium pressure of 0.01 mbar; (a) H-Y(5); (b) H-Y(18); (c) MOR(6.7); (d) MOR(10); (e) H-ZSM-5(52).

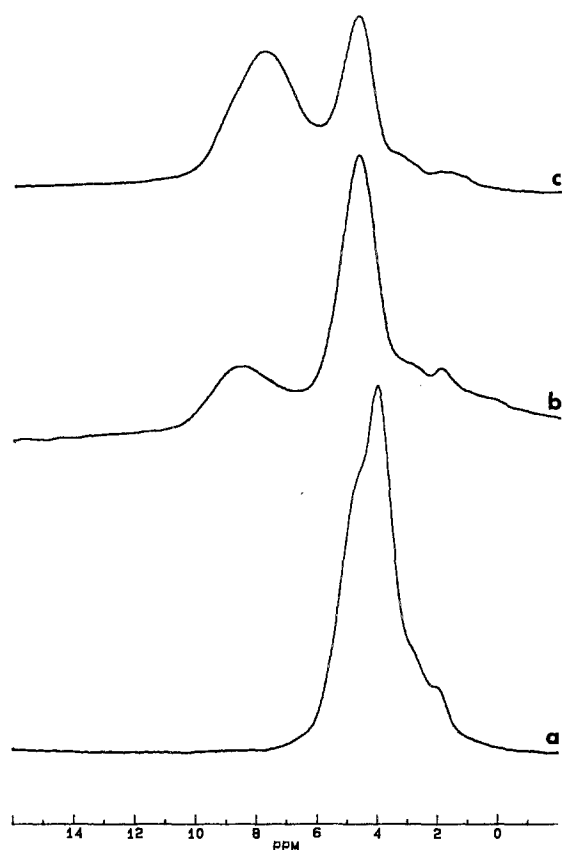


Fig. 6. ^1H MAS NMR spectra of H-Y(5) before (a) and upon adsorption of CD_3CN at an equilibrium pressures of 0.01 mbar (b) and 1 mbar (c).

number of covered LF protons in the FAU structure (here CCl_3CN is adsorbed) indicating weaker acidity of the LF proton. On the other hand, higher equilibrium pressure of the bases, corresponding with higher loading, does not influence the spectra of the other zeolites investigated.

Table 3 recapitulates the results of the NMR measurements. In good agreement with the IR results the extra chemical shift upon adsorption changes with the Si/Al ratio and does not seem to be influenced to a large extent by structural parameters (compare, for instance, ZSM-5 and H-Y(18) in table 3). Microcalorimetric measurements of ammonia on these types of zeolites (FAU [27], MOR [28], MFI [22]) could suggest some

Table 4

Some characteristic heats of chemisorption of ammonia, Q in kJ/mol, on zeolites with different pore size

Sample	Si/T ratio	Pore diameter (nm)	Q^a	Ref.
H-ZSM-5	52	0.6	140	[18]
H-Fe-MFI	32	0.6	130	[18]
H-MOR	18	0.67	140	[24]
H-FAU	12	1.2	125	[23]

^a Values measured on the same microcalorimetric apparatus.

higher acidic strength for the strongest proton in MFI and MOR type zeolites compared to the highly dealuminated FAU because of an increased heat of chemisorption (see table 4). However, this difference of about 15 kJ/mol between FAU and MFI may be due to a large extent to a pore size effect even for such a small molecule like ammonia [29]. Consequently, the spectroscopic results and microcalorimetric measurements are not in disagreement quite in contrast to what could be expected.

4. Conclusions

– The change of the ^1H MAS NMR chemical shift of a signal ascribed to the bridged hydroxyl groups in a zeolite upon adsorption of a weak base depends on the Si/Al ratio of the zeolite skeleton. The Si/Al ratios of ZSM-5, MOR(10) and HY(18) are above the value where no Al is in the second coordination sphere of the Si–OH–Al group. There the highest acid strengths can be expected, based on the NMR results.

– This is confirmed by comparing the changes of the OD bending modes upon adsorption of a base. It is the lattice chemistry which mainly influences the acidity. Most important aspects are the Si/Al ratio or the nature of the T atom in the same structure (Fe).

– The values of the changes of the OH stretching frequency in IR are more complicated because of the resonance with the OH bending overtones and an overlap of the HF and LF bands (in HY). But these shifts follow the same correlation as found in the NMR.

– A pore size effect has to be taken into account if the heats of chemisorption of bases and the catalytic

Table 3

^1H MAS NMR shifts, δ_{H} , in ppm, of different zeolites and their changes, $\Delta\delta_{\text{H}}$, upon adsorption of CCl_3CN and CD_3CN

Sample	δ_{H} before adsorption	δ_{H} after CCl_3CN adsorption	$\Delta\delta_{\text{H}}$ CCl_3CN	δ_{H} after CD_3CN adsorption	$\Delta\delta_{\text{H}}$ CD_3CN
H-ZSM-5(52)	4.1	9.0	4.9	11.2	7.1
H-Y(18)	4.2	9.1	4.9	11.2	7.0
	4.7	–	–	–	–
H-MOR(10)	4.2	8.9	4.7	10.9	6.7
H-MOR(6.7)	4.1	8.5	4.4	10.3	6.2
H-Y(5)	4.1	8.5	4.4	10.5	6.4
	4.7	7.7	3.0	9.0	4.3

behaviour of acidic zeolites with the same topological Al density are compared.

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