^{1}H broad-line and MAS NMR: application to the study of acid sites of desilicated zeolite ZSM-5

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Broad-line ^{1}H NMR study of desilicated zeolite ZSM-5 was carried out as a function of the number of adsorbed water molecules in amounts lower than or equal to that of the Brønsted acid sites. The dissociation coefficient of the acid OH groups, currently associated with the acid strength, was shown not to be affected by the selective removal of Si from the zeolite ZSM-5 framework which resulted in more Brønsted acid sites per unit surface area. On the other hand, by using MAS NMR, bridging Brønsted acid sites hydrogen-bonded to the zeolite framework were identified on the "anhydrous" surface of the desilicated ZSM-5. Moreover, MAS NMR spectra of the desilicated zeolite partially rehydrated showed the presence of some Lewis acid sites.

Keywords: solid state proton NMR; zeolite ZSM-5; desilication; surface acidity

1. Introduction

The Si/Al ratio of a silica-rich zeolite decreases by selective removal of framework silicon, using sodium carbonate as desilicating agent [1–3]. Although the removal of Si may be important, the degree of crystallinity and hence the zeolite structure are only slightly affected [1]. New micropores are created, which are slightly narrower than those of the parent zeolite [1,2]. However, upon activation at high temperature, a healing process occurs within the treated material framework, resulting in a slightly broader curve of micropore size distribution [2]. If the loss of Si upon desilication is limited to 40% of its original content, the tetrahedral Al sites are almost not affected by the desilication [1]. This results in a significantly enhanced cation exchange capacity per weight [2]. Moreover, the acid forms of these zeolites, if properly stabilized by (for instance) incorporation of lanthanum

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[4], may exhibit catalytic activity and selectivity which are quite different from those of the parent zeolites. Therefore, the study of the surface acidity of these desilicated materials appears interesting.

Brønsted acid sites in solids can be studied by various techniques [5]. ^{1}H NMR has been used in the high resolution magic angle sample spinning (MAS) mode [4–8] and the broad-line mode [9–11]. ^{1}H MAS NMR is essential for identifying and quantifying the OH group of different natures and, more generally, the Brønsted acid sites and some framework defects. However, drawing conclusions on the acid strength from MAS spectra is a difficult task [11]. Broad-line NMR has been proposed to provide a scale of Brønsted acid strength [9], based mainly on the concentration of hydroxonium ions formed when water interacts as a base with the Brønsted acid OH sites (bas). The ionization coefficient is the number of hydroxonium ions per base (H_3O^+/bas) when the number of interacting water molecules per base (ads. H_2O/bas) is equal to 1.

The objective of this work is, by using both ^{1}H NMR techniques [6–11], to investigate the strength of the Brønsted acid sites of two samples: a zeolite ZSM-5 and the same modified by desilication with sodium carbonate [1–3]. MAS NMR of ^{1}H performed on the "anhydrous" and partially rehydrated forms of the zeolites, is also used to identify the new acid sites eventually formed by the desilication.

2. Experimental

2.1. PREPARATION OF THE ZEOLITE SAMPLES

The parent zeolite H-ZSM-5 (denoted as H-Z) was prepared from the commercial zeolite Na-ZSM-5 (PZ 2/30 Na, powder, Na-form, from Chemie Uetikon AG, Switzerland). The ammonium form of the zeolite ZSM-5 was obtained by ion exchange according to the literature procedure [12], then converted to the acid form by thermal treatment as described below.

The desilicated H-form sample (denoted as H-TZ) was prepared according to the following procedure [3]: 5.0 g of the commercial zeolite Na-ZSM-5 were placed into a Teflon beaker, containing 150 cm^3 of 0.8 mol dm^{-3} sodium carbonate and 0.01 mol dm^{-3} sodium hydroxide solution (pH of the solution ≈ 11.8). The suspension was heated to 80°C for 4 h under moderate stirring. Then, it was allowed to settle, and the liquid was rapidly removed by filtration. A fresh volume of sodium carbonate and NaOH solution was added, and the suspension was stirred again very mildly at 80°C for a further 4 h. The same procedure was repeated a third time so that the entire operation lasted 12 h. Then the suspension was filtered, and the solid washed on the filter several times. The product, called Na-TZ, was dried in an oven at 120°C overnight. The H-TZ sample was obtained from the Na-TZ by applying the same treatment procedure as reported for the H-Z parent zeolite [12]. In particular, both (ammonium form) Z and TZ materials were dried at 120°C overnight and finally calcined at 450°C for 10 h.

2.2. CHARACTERIZATION OF THE ZEOLITE SAMPLES

The samples were characterized by elemental analysis (AAS: atomic absorption spectrometry), X-ray powder diffraction and BET measurements by nitrogen adsorption. X-ray powder diffraction was used to identify the structure of the zeolites and to determine the degree of crystallinity of the materials prepared, using the technique developed previously [12]. The BET surface area and the volume of nitrogen adsorbed (total volume adsorbed and the volume adsorbed by the micropores, the latter hereafter referred to as MP) were determined by means of a Micromeritics ASAP 2000 model apparatus.

Table 1 reports the main physico-chemical properties of the samples studied, and in particular, their chemical compositions which were determined by AAS. The Si/Al ratio was determined by chemical means and by NMR. The similarity of the two values proves that the sample does not contain extra-framework aluminum. The Si/Al ratio could be used to calculate the Al content per unit cell (uc) in the zeolite before desilication in accordance with the well-known basic formula for the zeolite ZSM-5 as follows: $Na_n[Al_nSi_{96-n}O_{192}] \sim 16H_2O$. However, after desilication, although the Si/Al ratio has significantly decreased, the number of Al atoms per unit cell remains the same, and the above formula is not usable.

The treatment with sodium carbonate results in a selective removal of framework Si atoms leaving behind vacancies which are subsequently modified by some healing process [1]. It has also been shown [1,2] that no dealumination occurs under the desilication conditions used. Therefore, the total content of framework Al atoms remains unchanged. As the BET surface area does not vary significantly upon desilication (table 1), the number of Al sites per surface area unit also remains unchanged. To take advantage of such a situation which allows us to relate these results to the properties of the materials involving surface contact phenomena (catalysis or ion exchange), the data on acidity will be conveniently expressed hereafter in moles per m^2.

For NMR studies, the zeolite sample (0.5 g) was pretreated at 400°C in "shallow

Table 1
Physico-chemical properties of the zeolite samples studied

Sample	DC[a]	BET[b]	Vol. N_2[c]		Chemical composition[d]			
			total	MP	Al_2O_3	Na_2O	SiO_2	Si/Al[e]
H-Z	100	402	0.321	0.108	4.5	0.35	95.1	18.0
H-TZ	89	406	0.418	0.105	7.3	0.33	92.4	10.7

[a] Degree of crystallinity, expressed in %.
[b] BET surface area, expressed in m^2/g.
[c] Volume of adsorbed nitrogen, expressed in cm^3/g.
[d] Expressed in wt% (dried oxide basis).
[e] Atomic ratio.

bed" conditions (vacuum, heating rate = 12°C h^{-1}, sealing) as described previously [9]. It is currently believed that shallow-bed treatment can preserve the original structure of the zeolite material. Then water was adsorbed stepwise at low pressure and ambient temperature, the amount of water being monitored gravimetrically. The distribution of the adsorbed water was homogenized by heating at 120°C overnight after which the sample-containing ampoules were sealed under vacuum.

(i) ^{1}H MAS NMR spectra of the "anhydrous" samples (i.e. without molecular water, but still hydroxylated) and of the same onto which water, at several different concentrations, was adsorbed, were collected with a MSL 400 MHz Bruker spectrometer with a 3 kHz spinning rate. The chemical shifts of protons are given in this paper without any susceptibility correction relative to liquid TMS as external reference. The repetition time was between 5 and 100 s. The spectra of the "anhydrous" H-Z and H-TZ samples were simulated so as to calculate the relative distribution of hydroxyl protons from SiOH, AlOH and bridging ZOH (or SiO (H)Al as defined in ref. [9]) taking into consideration the spinning side bands arising from each peak.

(ii) Broad line ^{1}H NMR (4 K) spectra of each of the samples for all the concentrations of water adsorbed, were collected with a 60 MHz spectrometer using a home made probe, at the temperature of liquid helium (4 K). Half derivative adsorption spectra data were obtained and simulated by the method developed previously [11] which allowed the calculation of the concentration of each different oxygen protonated species contributing to the shape of the simulated spectra. The following magnetic configurations of spin 1/2 were identified in basis of the dipolar interaction between two proton spins separated by a distance r [9–11]:

- two-spin configuration, for H atoms of water molecules remaining which do not undergo interactions with OH groups, and also for some OH groups;
- three-spin at the apices of an equilateral triangle, for hydroxonium ions;
- three-spin at the apices of an isosceles triangle, for groups formed from a water molecule hydrogen-bonded to an OH or for hydroxonium ions hydrogen-bonded to oxygen atoms of the framework;
- a Gaussian function to describe the resonance of a set of OH groups;
- a Lorentzian function representing some particular sets of diluted OH.

3. Results and discussion

Figs. 1 and 2 show the simulated curves superimposed on the corresponding ^{1}H MAS NMR spectra of the "anhydrous" forms of the parent zeolite ZSM-5 (H-Z) and the treated sample (H-TZ), respectively. In both spectra, a shoulder was present on the low-field edge of the 3.9–4.3 ppm signal, as described by Beck et al. [13]. These authors and Brunner et al. [14,15] showed that such a shoulder or a broad signal at this position was narrowed when the temperature of the sample was lowered to 125 K, resulting in a ca. 400 Hz wide signal at 6.7–7.0 ppm. A similar, relatively

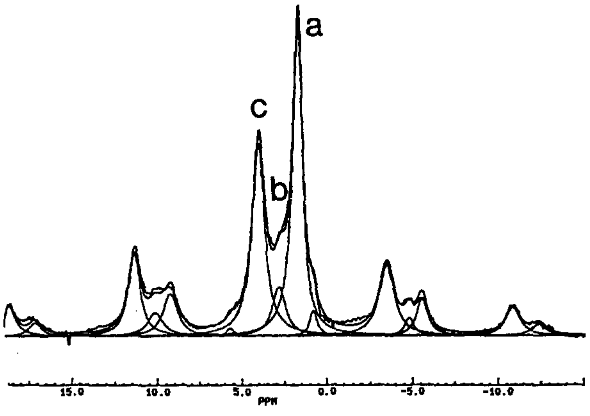

Fig. 1. ^{1}H MAS NMR for the anhydrous form of H-Z zeolite and corresponding decomposition curves. Peaks a, b and c are assigned to the Si–OH groups, the Al–OH and the Z–OH acid sites, respectively.

narrow signal, was present in the spectrum of the H-TZ obtained at room temperature (fig. 2). However, this signal was practically negligible for the H-Z sample (fig. 1). The assignment of this signal has been recently discussed [14–18]. It presumably corresponds to Brønsted acid sites hydrogen-bonded to framework oxygen atoms, denoted as type 2 sites (those of type 1 resonating at about 4 ppm) [15]. Since no NMR signal characteristic of molecular water was detected at 4 K (no doublet for a two-spin configuration), the signal observed at 6.7–7.0 ppm cannot be confused with the one at 6.5 ppm, which is assigned to molecular water on Lewis acid sites [18]. The type 2 Brønsted acid sites will be called hereafter ZOH* (simply for convenience). The presence of this 6.8 ppm signal in the spectrum of the anhy-

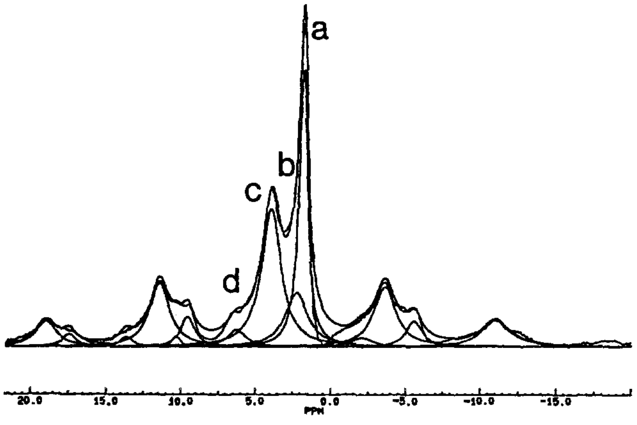

Fig. 2. ^{1}H MAS NMR for the anhydrous form of H-TZ zeolite and corresponding decomposition curves. Peaks a, b, c and d are assigned to the Si–OH groups, the Al–OH, the Z–OH and the Z–OH* acid sites, respectively.

drous H-TZ sample (whereas it is negligible in the spectrum of H-Z) shows then that the whole process of desilication, including the subsequent healing, creates new acid groups, ZOH*, probably hydrogen-bonded to the lattice oxygens. The formation of hydrogen bonds in these ZOH* sites may be favored by the presence of structural defects on the zeolite surface as in the case of a dealuminated or desilicated material. Si removal may occur at two different locations of the (Na) zeolite framework, as shown in fig. 3: (a) In a zone rich in Si, several terminal groups are formed with the departure of a Si atom. Those silanol groups normally do not exhibit any significant acid strength. In this case the healing must create the more or less deformed siloxane bonds. However, this does not involve all the newly formed SiOH groups, thus contributing to slightly increasing the number of these silanols, from 1.10×10^{-6} to 1.30×10^{-6} mol/m^2 (table 2). (b) If the Si atom to be removed is part of an anionic ZO$^-$ site (fig. 3b), first the ZO$^-$ is destroyed, then, in the Na$^+$ aqueous environment, most of such Al atoms would become finally Al$^-$ tetracoordinated by oxygen atoms. Such a reinsertion of Al species into the zeolite framework is probably promoted by Na$^+$ ions and water (steam) [19]. Healing goes to completion when the desilicated sample is heated at high temperature (>250°C) [1,2]. Therefore, ZO$^-$ groups are recreated from the tetracoordinated Al$^-$ through a yet unknown healing process.

Table 2 shows that the initial Al(OH) concentration in HZ (0.73×10^{-6} mol/m^2) is approximately equal to the sum of the Al(OH) concentration (0.26×10^{-6} mol/m^2) and that of the ZOH* created (0.43×10^{-6} mol/m^2) in HTZ. This result would appear to prove that the overall process (desilication + healing) concerns mainly the neighbourhood of the Al(OH) defects, transforming them into

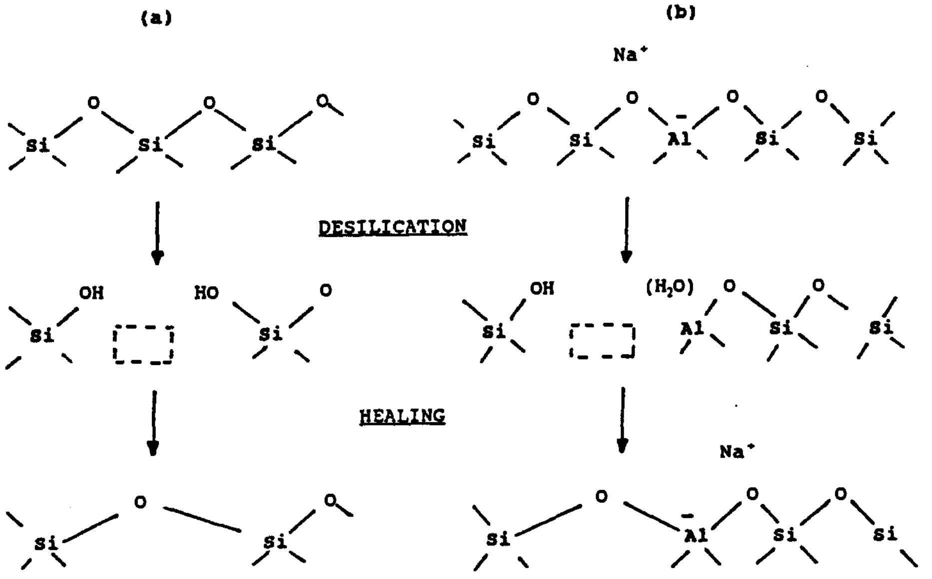

Fig. 3. Proposed mechanisms for the desilication and subsequent healing of H-Z.

Table 2
^{1}H MAS NMR data: distribution of oxygen-protonated species groups of "anhydrous" zeolite samples (data expressed in 10^{-6} mol/m^2)

Sample	H-Z	H-TZ
Al atoms	2.19 ± 0.20	2.19 ± 0.20
SiOH	1.10 ± 0.08	1.30 ± 0.10
AlOH	0.73 ± 0.10	0.26 ± 0.05
ZOH	1.47 ± 0.10	1.50 ± 0.10
ZOH*	(negligible)	0.43 ± 0.05
total OH	3.30	3.49
acidic OH	1.47 ± 0.10	1.93 ± 0.30

[a] ZOH* has probably the following configuration: $ZOH \cdots O_z$ (O_z being a framework oxygen [14–16]).

bridged Al(OH)Si sites. Whatever the exact mechanism, the concentration of acid sites is greater in HTZ than in HZ. These results explain why desilicated Y and X zeolites exhibit enhanced cation exchange capacities [2]. They also indicate that no framework Al atoms are extracted by the sodium carbonate solution, in agreement with previous work [1,2].

When water is loaded into the NMR tube, several oxyprotonated species can be observed: OH groups, H_2O molecules and other species which originate from the following interactions [9–11]:

$$\text{Z–OH (or ZOH}^*) + H_2O \rightleftharpoons \text{Z–OH} \cdots OH_2 \rightleftharpoons \text{Z–O}^- + H_3O^+$$

In table 3 are reported the quantities of these species as functions of the amount of water loaded. Simulation of the HZ spectra shows that:

– When the concentration of adsorbed water is less than or equal to that of ZOH, all these acid sites interact with the water molecules, either by hydrogen bonding or giving H_3O^+. This is in agreement with the results obtained for other zeolites [10]. The dissociation coefficient of these OH groups is 0.2 when the number of water molecules is equal to that of ZOH.

– Free water molecules (i.e. molecules not interacting with the OH groups) can be detected when the water concentration is greater than that of OH.

– In contradiction to results on zeolites without defects, the H_3O^+ concentration increases with the degree of hydration.

In contrast with what is observed with the parent HZ zeolite, a signal at 6.8 ppm is seen in the ^{1}H MAS NMR spectrum of HTZ (fig. 4), indicating thus that a few water molecules are bonded to the Lewis acid sites from the start of adsorption. This is confirmed by NMR at 4 K, which demonstrates that there are water molecules not interacting with the OH groups right from the start of adsorption

Table 3
Broad-line ^1H NMR data: distribution of oxygen-protonated species groups (data expressed in 10^{-6} mol/m^2) of the zeolite samples after adsorption of water

No. of adsorbed water molecules [a]	No. of H_3O^+ [a]	No. of $H_2O \cdots HOZ$ groups [a,b]	No. of free OH groups [a]	No. of free H_2O molecules [a]	IC[c]
H-Z zeolite					
1.1	0.33	1.33	0.50	0	
1.4	0.20	1.22	1.84	0	
2.2	0.38	1.82	1.08	0	0.2[d]
4.5	0.74	1.66	1.24	2.0	
H-TZ zeolite					
1.0	0.19	0.80	2.26	0.2	
2.2	0.42	1.54	1.75	0.2	0.2[d]
4.1	0.43	1.68	1.75	1.8	

[a] Accuracy according to ref. [9] for: No. of adsorbed water molecules at water loadings similar to those used in this work = ±5%; No. of H_3O^+ ions = ±10%; No. of $H_2O \cdots HOZ$ groups = ±10%; No. of free H_2O molecules = ±10%.

[b] ZOH: includes ZOH and eventually ZOH*.

[c] Ionization coefficient = No. of H_3O^+ per initial acidic OH groups.

[d] Estimated accuracy = ±20%.

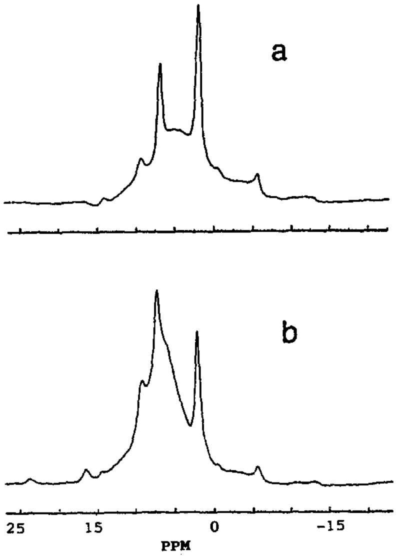

Fig. 4. ^1H MAS NMR spectra of the H-TZ zeolite with two different (high) water loadings: (a) 3.6×10^{-6} mol/m^2 and (b) 6.6×10^{-6} mol/m^2.

(fig. 5 and table 3). These molecules represent about 10% of the water adsorbed and 2% of the total number of atoms in the sample, when the number of molecules adsorbed is 2.2×10^{-6} mol/m^2, i.e. slightly greater than the total number of Brønsted acid sites (1.95×10^{-6} mol/m^2). These concentrations are in fair agreement with those deduced from the MAS NMR spectra. It is believed that few Al atoms coordinately bound to water are created during the desilication process (fig. 3b), resulting in these Lewis acid sites during the shallow-bed pretreatment [10]. Remy et al. [20] also found by X-ray photoelectron spectroscopy such three-coordinated Al atoms in dealuminated mordenites.

Let us consider now the situation where the number of water molecules loaded is about equal to that of the Brønsted acid sites of the zeolite material. As mentioned earlier, the number of free water molecules present in the sample is either nil (HZ) or weak for water on Lewis acid sites (H-TZ). It is proposed in this case to use the value of the ionization coefficient in the setting-up of the acidity scale [9]. These values are in agreement with that of 0.2 determined in ref. [9] for the ionization coefficient of the bridged ZOH sites in some HY zeolites. However, it is lower than for other samples of HZSM-5 and H-mordenite types [21] for which it has been found equal to ca. 0.3. Since there is almost no change in the ionization coefficient, it is possible to state that the ZOH* sites identified in the "anhydrous" form of the desilicated zeolite are easily converted back to the bridged ZOH sites during the rehydration phase.

The results of this work show that ^{1}H MAS NMR and ^{1}H broad-line NMR are very useful techniques for the study of the acid sites of desilicated zeolites. More detailed studies will be done, this time in conjunction with more conventional techniques such as the temperature programmed adsorption/desorption of a base or IR spectroscopy [22,23]. In particular, a detailed study of the Lewis acid sites of desilicated zeolites is under way.

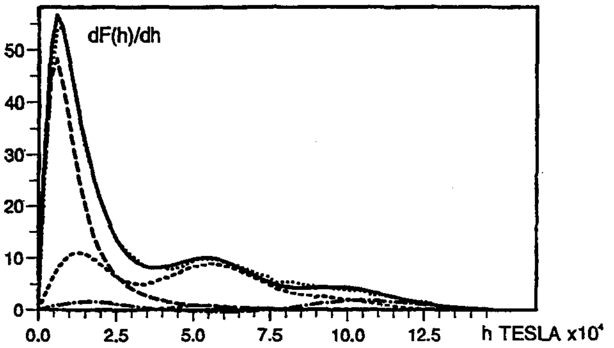

Fig. 5. Broad-line ^{1}H NMR spectrum (half derivative) of the H-TZ sample with a water loading of 1.0×10^{-6} mol/m^2. (——) calculated; (···) experimental; (– – –) Lorentzian function; (- - -) isoceles and (– · –) equilateral.

4. Conclusion

Broad-line ^1H NMR shows that the selective removal of Si from the zeolite ZSM-5 surface results in a few more silanol groups (i.e. more structural defects) and significantly more Brønsted acid sites per unit surface area. The strength of the latter sites, determined through the ionization coefficient, does not differ significantly from that of the normal bridging Brønsted acid sites in zeolites. Some Lewis acid sites, produced by the desilication treatment, are detected by ^1H MAS NMR during the rehydration phase.

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