^{1}H MAS NMR STUDIES ON THE ACIDITY OF ZEOLITES

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Proton magic-angle-spinning nuclear magnetic resonance (^{1}H MAS NMR) spectra contain quantitative information about Brønsted acidity and structure defects in zeolites. The strength of acidity of bridging OH groups increases with the Si/Al ratio from 1.4 to 7 but remains constant above Si/Al ≈ 10. Two signals of acidic hydroxyl protons observed in zeolites HY are correlated with the so-called high- and low-frequency band in infrared spectroscopy.

1. Introduction

With respect to the Brønsted acidity of surface OH groups, one has to distinguish between two independent quantities, both measurable by ^{1}H MAS NMR [1]: S_a, the strength of acidity, which is defined as the ease of proton transfer from a surface site to an adsorbed base and A_a, the amount of acid, which is given by the concentration of the respective acid sites. According to ab initio quantum chemical calculations [2], S_a increases with decreasing electronic charge of the hydrogen atoms, that means with a larger value for the chemical shift δ_H of the proton magnetic resonance. On the other hand, the NMR intensity is directly proportional to A_a.

The ^{1}H MAS NMR spectrum of unloaded zeolites consists in general of four lines [1]: Line (a) at 1.3–2.3 ppm is caused by non-acidic OH groups at the outer surface of zeolite crystals (terminal OH groups), at lattice defects and on amorphous components of the zeolites. Line (b) at 3.8–4.6 ppm is ascribed to acidic OH groups, which are known to be of bridging type. Line (c) at 4.8–5.8 ppm appears additionally in zeolites of faujasite type and is ascribed also to acidic bridging OH groups. Line (d) at 7 ppm is due to residual amounts of ammonium ions.

In the present work the ^{1}H MAS NMR spectra of unloaded zeolites and zeolites loaded with definite amounts of ammonia or deuterated pyridine are analysed to study the acidity and the extent of structure defects in hydrogen zeolites of faujasite and ZSM-5 type.

2. Experimental

All ^{1}H MAS NMR spectra were measured at 270 MHz and at a rotation speed of the fused glass ampoules of 3 kHz using a home-made pulse spectrometer in Leipzig. The samples were pretreated according to deep bed conditions: The zeolite crystals were heated in an open glass tube (6 mm diameter, 10 mm height of the zeolite layer) under atmospheric pressure at a rate of 100 K/h up to 400°C. After keeping the samples for 2 h at this temperature they were evacuated to a pressure below 0.01 Pa for 20 h and sealed off. The total concentration of protons for each sample was determined by measuring the free induction decay after a $\pi/2$ pulse and comparing its initial value with that of a standard.

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3. Results and discussion

3.1. Zeolites of ZMS-5 type

The samples under study are characterized in table 1. In fig. 1 ^{1}H MAS NMR spectra of some unloaded samples are shown. Values for the concentration of protons giving rise to lines (a) and (b) and those of aluminium atoms are collected in table 2. The number of terminal OH groups is calculated by the equation $n_T = 1.2 \times 10^{19}/d$, where d denotes the mean diameter of the zeolite crystallites in μm which is given in table 1.

Table 2
Concentration of protons giving rise to lines (a) and (b), number n_T of terminal OH groups calculated from the diameter of the crystallites given in table 1, and the number of aluminium atoms in the zeolite framework. All values are given in 10^{19} per gram. The experimental error is ±10%

Sample	Protons of line (a)	Protons of line (b)	n_T	Al atoms
H-ZSM-5/TPA	36	24	0.7	23
H-ZSM-5/But	5	35	1.1	31
H-ZSM-5/Pro	4	32	1.0	27
H-ZSM-5/free	6	49	0.3	58

Table 1
Characterization of the H-ZSM-5 samples: The template molecule, the reference for the synthesis, the mean diameter of the crystallites, and the Si/Al ratio determined by ^{27}Al NMR [3]. All samples were hydrogen exchanged by a treatment with dilute HCl

Specimen	Reference	Template	Diameter (μm)	Si/Al
ZSM-5/TPA	US-P 3702 886	TPA	1.7	40
ZSM-5/But	DE-OS 2442 240	*n*-butylamine	1.1	30
ZSM-5/Pro	DE-OS 2442 240	*n*-propylamine	1.2	35
ZSM-5/free	DD-WP 207 186	none	3.2	15

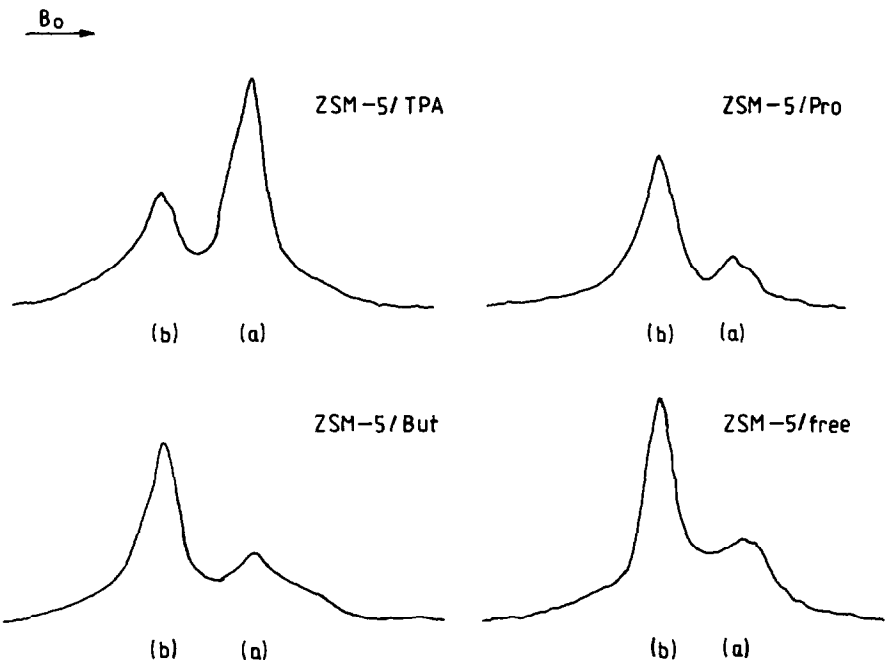

Fig. 1. ^{1}H MAS NMR spectra of unloaded samples of H-ZSM-5.

The concentration of non-acidic hydroxyl groups (line (a)) is less than 10% of the total concentration of OH groups, except in sample ZSM-5/TPA where the zeolite specimen was prepared using tetrapropylammonium iodide. In accordance with a similar result for zeolites HY [1] the concentration of non-acidic hydroxyl groups is much greater than the value which follows from the number of terminal OH groups. This is contrary to the result of Qin et al. [4] who ascribed the infrared band of non-acidic hydroxyl groups in ZSM-5 samples only to the terminal OH groups. In accordance with Datka [5] we ascribe the extremely high concentration of 36×10^{19} SiOH groups per gram for sample ZSM-5/TPA to defects of the zeolite framework produced by the decomposition of the template.

The signals due to bridging OH groups (line (b)) can be removed through an interaction with adsorbed deuterated pyridine. A reammonation of the samples gives rise to an increase of the intensity of line (d) and a decrease of that of line (b). For a loading corresponding to 50×10^{19} ammonia molecules per gram of zeolite, line (b) of sample ZSM-5/free disappears (cf. fig. 2) which is in excellent agreement with the value for the number of bridging OH groups determined directly from the intensity of line (b) of the unloaded sample (cf. table 2).

Summarizing, we can state that for the specimens listed in table 1 the number of bridging OH groups is equal to the number of aluminium atoms, and that due to their accessibility (pyridine) all bridging hydroxyl groups should be able to take part in catalytic reactions. For the ZSM-5 prepared by the use of tetrapropylammonium iodide an extremely high concentration of lattice defects is present.

3.2. Zeolites HY

The stretching vibrations of bridging hydroxyl groups in zeolites of faujasite type give rise to two separate signals in infrared spectroscopy, the so-called HF band at 3650 cm^{-1} and the LF band at 3540 cm^{-1} [6]. In the ^1H MAS NMR spectra of these zeolites we have also observed [1] two lines caused by bridiging hydroxyl groups which were denoted as (b) and (c), and the question arises whether line (b) corresponds to the HF band and therefore line (c) to the LF band or vice versa. The ^1H MAS NMR spectra of the unloaded samples for ammonium exchanges of 36, 64, and 90% are shown in fig. 3. In all spectra the signals of SiOH groups (line (a) at 1.8 ppm) and of residual ammonium ions (line (d) at 7 ppm) can be seen. For an exchange of 36% the bridging OH groups give rise to a line (b) at 4.2 ppm. For values of the exchange degree greater than ≈50%, an additional line (line (c) at 5.2 ppm) appears with increasing intensity, so that for 90% where the total concentration of hydroxyl groups is 3.7 per 1/8 unit cell, 2.2 OH groups give rise to line (b) and 1.1 OH groups to line (c). The sum (3.3) is nearly equal to the concentration of aluminium atoms in lattice sites (3.7 Al per 1/8 unit cell) which was determined by ^{27}Al NMR (cf. ref. [3]). In analogy to the interpretation of the HF and LF stretching vibrations [7] we suggest that the larger shift of line (c) is not due to a higher strength of acidity, but is related to the smallness of the cages (sodalite units) where these bridging OH groups are located.

To prove this suggestion we have loaded the sample with an ammonium exchange of 90% (zeolite 90 HY) with definite amounts of deuterated pyridine,

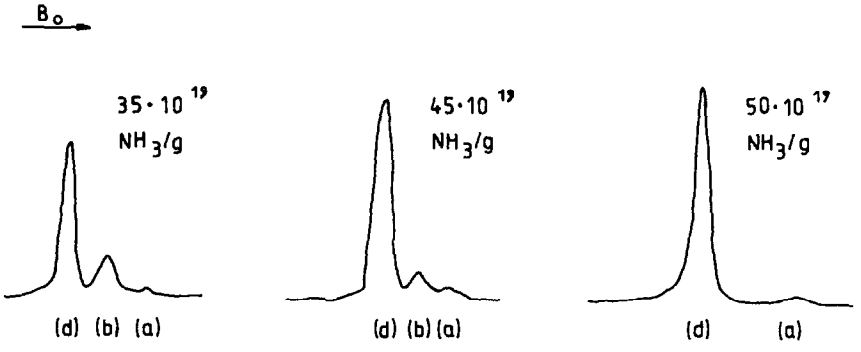

Fig. 2. ^1H MAS NMR spectra of the zeolite H-ZSM-5/free loaded with an increasing amount of ammonia.

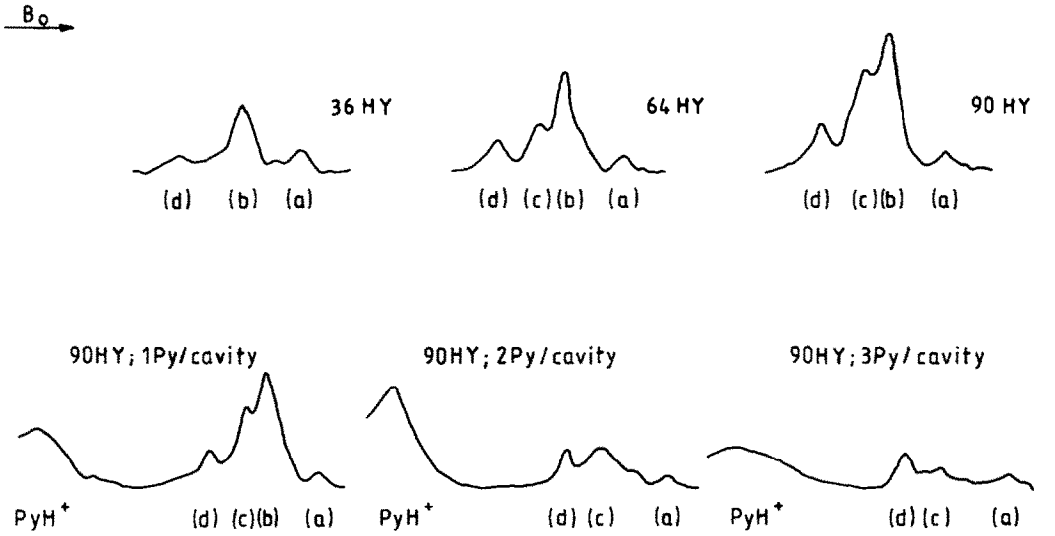

Fig. 3. ^{1}H MAS NMR spectra of various unloaded ammonium exchanged zeolites NaY after deep bed pretreatment and spectra of the zeolite 90 HY after loading with deuterated pyridine. The loading is given in molecules per 1/8 unit cell.

since an adsorption of pyridine on a bridging OH group leads to the formation of a pyridinium ion and consequently to a shift of the proton magnetic resonance line to 12–16 ppm [8]. As can be seen in fig. 3, small concentrations of pyridine give rise to the signal of pyridinium ions at 16 ppm with a corresponding decrease of the intensity of line (b). At higher concentrations, at first line (b) disappears and finally also line (c). Hence we must conclude that both sorts of bridging OH groups are accessible for pyridine and that the interaction of pyridine with the bridging OH groups of line (c) is less than with those of line (b).

Summarizing, we can correlate the infrared stretching and ^{1}H MAS NMR frequencies of zeolites HY as follows: Line (a) corresponds to the non-acidic OH groups with a stretching vibration frequency of 3740 cm^{-1}, line (b) to the bridging OH groups located in the large cavities giving rise to the so-called HF band at 3650 cm^{-1}, and line (c) to the bridging OH groups located in the small cavities (sodalite units) giving rise to the so-called LF band at 3540 cm^{-1}. Since in contrast to infrared spectroscopy, the intensity (area) of a ^{1}H NMR line is directly proportional to the corresponding concentration of protons (the factor of proportionality is a constant and does *not* depend on the position of the line) it becomes possible to repeat infrared studies (cf. e.g. refs. [6,7]) by using the new ^{1}H MAS NMR method and to adopt the interpretation of frequency shifts to the NMR measurements with the most important advantage that quantitative results may be derived concerning the concentration of the species under study.

3.3. Strength of acidity of various zeolites

It is well known that the strength of acidity of bridging OH groups depends on the Sanderson intermediate electronegativity which may be changed through a substitution of aluminium by phosphorus or boron [9,10] or by the silicon-to-aluminium ratio. In an attempt to rationalize stretching frequencies of lattice hydroxyl groups in hydrogen zeolites [7], a linear dependence of the frequency of unperturbed bridging OH groups (the HF band) on Sanderson's intermediate electronegativity of the zeolites was found. In fig. 4 we have plotted for some examples taken from ref. [7] values for ν_{OH} as a function of the ratio Si/Al. In this same figure our results for the chemical shift δ_H of line (b) in the ^{1}H MAS NMR spectra of hydrogen zeolites (various faujasites, mordenites and ZSM-5) are presented. The faujasite samples were pretreated under shallow bed conditions. All other samples were pretreated according to the

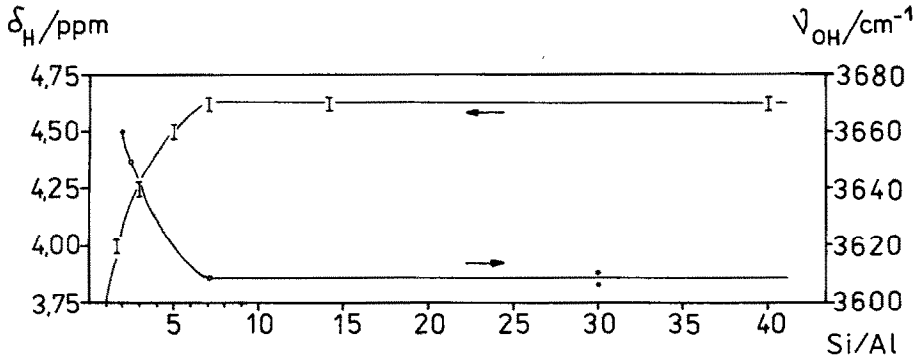

Fig. 4. Values for the chemical shift δ_H of line (b) in the ^1H MAS NMR spectra of various zeolites as a function of the Si/Al ratio. For comparison some values for the stretching frequency of the HF band or the corresponding band in the infrared spectra taken from ref. [7] are included.

deep bed procedure described above, and for the measurement of the chemical shift δ_H, line (d) at 7 ppm was used as an internal reference. As one can see, after a sharp increase, the chemical shift δ_H remains constant within the limits of accuracy (±0.1 ppm) for silicon-to-aluminium ratios greater than ≈10.

In our former work [1] we have compared the catalytic activity of various zeolites HY (lines (b) and (c)) and H-mordenites (line (b)), expressed by the rate constant k_1 of cumene cracking with the concentration of bridging OH groups $c^{(b+c)}$, $c^{(b)}$ and $c^{(c)}$. According to the results of section 3.2 of the present work, we must now state that the OH groups of line (b) are by no means less active than those of line (c). However, for the zeolites HY under study the silicon-to-aluminium ratio is only 2.6, which means that the strength of acidity of their bridging OH groups located in the large cavities is much smaller than that of the H-mordenites (Si/Al = 7). Hence we must conclude that the enhanced catalytic activity of the H-mordenites compared with zeolites HY having the same concentration of bridging OH groups located in the large cavities is due to the higher strength of acidity of their OH groups.

According to fig. 4 the strength of acidity of the bridging OH groups should be constant above a silicon-to-aluminium ratio of ≈10 and a further change of the catalytic activity must be due to sites which are not visible in the present ^1H MAS NMR spectra.

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