HIGHLY RESOLVED PROTON MAGNETIC RESONANCE SPECTRA OF HYDROXYL GROUPS IN HYDROGEN-ZEOLITES

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With magic angle spinning of glass ampoules containing dehydrated hydrogen-zeolites, four different proton magnetic resonance lines at 270 MHz could be separated. The line at highest magnetic field (1 8 ppm with respect to TMS) is due to non-acid OH groups formed on zeolite crystal surfaces (terminal hydroxyl groups) and at crystal defects. The two lines at medium field (3 9–4 6 and 4.8–5 6 ppm) are caused by the acid or so-called structural OH groups giving rise to low- and high-frequency bands in infrared spectra, and the major part of the signal at the lowest magnetic field (7.0–7.5 ppm) is attributed to residual NH_4^+ ions of the zeolite. An advantage of this technique compared with infrared spectroscopy is that the band areas are strictly proportional to the number of protons contributing to the signal.

1. Introduction

To evaluate the catalytic activity of a zeolite it is necessary to determine the nature, strength and distribution of the acid sites. Besides the well-established methods of titration [1] and infrared spectroscopy [2,3], high-resolution proton magnetic resonance spectroscopy can now be used [4–6] to yield valuable information about acid sites of Brønsted type (hydroxyl groups) of solid catalysts since this method does not suffer from two important difficulties, namely the influence of steric effects and the lack of a direct quantitative determination, that are characteristic of titration methods and of infrared spectroscopy, respectively. To obtain highly resolved proton magnetic resonance spectra it is necessary to rotate the samples in fused glass ampoules with a speed of some kHz around an axis which is inclined at the so-called magic angle (54.7°) with respect to the external magnetic field [7]. This line-narrowing procedure has been shown [8] to be effective also when the neighbouring nuclei have a quadrupole moment, which may occur for hydroxyl groups in zeolites if they are in the neighbourhood of aluminium.

In the present paper the resolution has been enhanced and the spectra thus found consist of up to four separated lines. Spectra of hydroxyl groups under the influence of adsorbed molecules of pyridine and ammonia indicate that the lines are due to non-acid OH groups, two sorts of acid hydroxyl groups and residual ammonium ions.

2. Experimental

Starting from a zeolite NaY (VEB Chemiekombinat Bitterfeld, GDR) with a Si/Al ratio of 2.6, the ammonium type was prepared by a cation exchange of

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88 ± 3% in an aqueous solution of ammonium nitrate according to Chu et al. [9]. One portion was pretreated under "deep bed" (DB) conditions: The powder was heated in an open glass tube (4 mm diameter, 6 mm length) under atmospheric pressure by raising the temperature at a rate of 100 K h^{-1} up to the chosen temperature of activation. After keeping the samples for two hours at this temperature, they were evacuated for twenty hours and sealed off. During this latter procedure the pressure decreased below 0.01 Pa. For another sample a procedure similar to the "shallow bed" (SB) condition was used for preparation: The sample was heated in vacuo at a rate of 10 K h^{-1} to the final temperature of activation and sealed off under vacuum. In what follows a sample prepared, for example, at a final temperature of 300°C under deep bed conditions is denoted as "300 DB". The adsorption of pyridine and ammonia was carried out at room temperature up to the saturation value. Only the samples loaded with ammonia at 1300 Pa were evacuated after the adsorption process to 1 Pa, to remove physically adsorbed ammonia.

Some of the highly resolved spectra and all intensity measurements for the determination of the number of OH groups, were carried out with an NMR pulse spectrometer at 90 MHz using the free induction decay after a $\pi/2$ pulse. The other highly resolved spectra were measured at 270 MHz using the WHH-4 pulse sequence (cf. ref. [10]) with 256 cycles of 24 μs recycle time and a repetition time of 4 s. In all measurements the rotation speed of the fused glass ampoules was 2.5 kHz. The proton magnetic resonance shifts are referred to TMS and are positive to lower field. The line observed at 1.8 ppm was used as an internal standard and measured with an accuracy of ±0.5 ppm via adamantane. A correction according to Michel et al. [11], considering susceptibility effects, could be neglected.

3. Results

The highly resolved proton magnetic resonance spectrum of a hydrogen-zeolite (300 SB) measured at 270 MHz is shown in fig. 1a. One can easily observe four lines at (a) 1.8, (b) 4.6, (c) 5.6, and (d) 7.2 ppm, the first having a full-half-linewidth ($\Delta\nu_{1/2}$) of 400 Hz. For higher values of the activation temperature

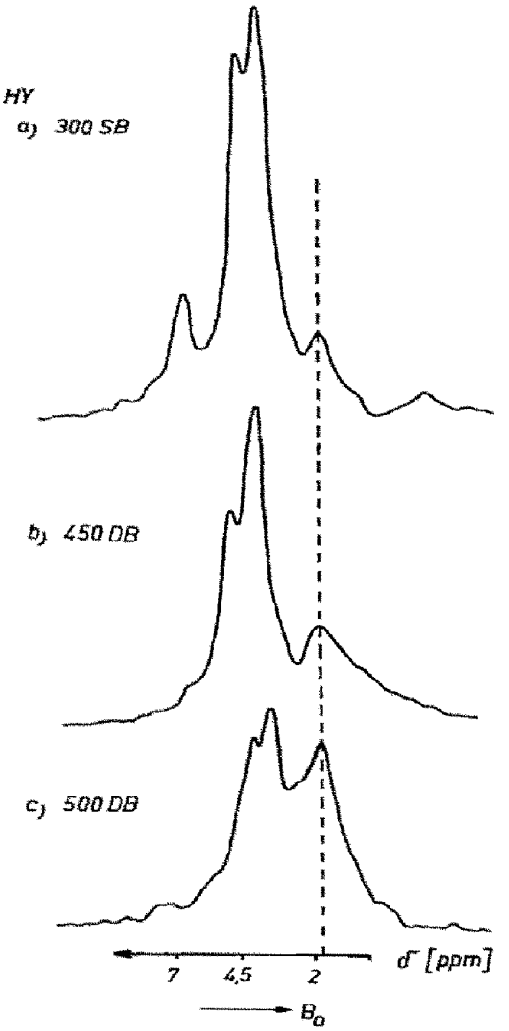

Fig. 1. MAS proton magnetic resonance spectra of HY zeolites measured at 270 MHz.

(450 DB and 500 DB) the intensities of lines (b) and (c) decrease and line (d) vanishes completely (cf. figs. 1b, 1c and table 1). The full-half-linewidth of line (a) increases with increasing activation temperature, its value is 800 Hz for 500 DB.

After loading the 300 DB sample with perdeuterated pyridine to the saturation value, only lines (b), (c) and (d) vanish, as can be seen in fig. 2a. This experimental finding is explained as follows: The mean residence time $\tau_{c\,OH}$ of a proton at an oxygen atom forming an OH group decreases from a value of ≈7

Table 1
Number n of protons per unit cell of HY zeolites contributing to the different proton magnetic resonance lines: (a): 1.8 ppm; (b) + (c) 3.0–5.6 ppm; (d): 7.0–7.5 ppm. The accuracy of the values is ±10%

Zeolite	n_a	$n_b + n_c$	n_d
300 SB	4.8	48	3.2
400 SB	4	46	3.2
300 DB	3.2	29	14
400 DB	3.6	28	8.8
450 DB	4.5	26	–
500 DB	6.0	16	–

ms for the unloaded 300 DB sample to ≈15 μs because of the interaction with the adsorbed (perdeuterated) pyridine molecules [12]. This enhanced mobility of the protons gives rise to a dramatic broadening of the corresponding proton magnetic resonance lines in the MAS spectra, since the linewidth $\Delta\nu_{1/2}$ is proportional to the expression [13]

$$2\tau_{c\,OH}/[1+(\omega_r\tau_{c\,OH})^2]+\tau_{c\,OH}/[1+(2\omega_r\tau_{c\,OH})^2]\,,$$

where $\omega_r/2\pi = 2.5$ kHz denotes the rotation speed of the sample. Introducing the above values, a broadening by a factor of about 20 should occur, making the lines unobservable.

To identify the line occurring at ≈7 ppm (line (d)), an ammonium-exchanged sample was measured without any heat pretreatment. The spectrum shown in fig. 2b exhibits two lines at 7 and 4.8 ppm which must be ascribed to the protons of the ammonium ions [14] and water [15], respectively. Therefore we can assume that line (d) in fig. 1a is caused by residual ammonium ions. In accordance with this interpretation, a loading of sample 300 DB with ammonia (cf. fig. 2c) decreases the intensity of lines (b) and (c) and increases that of line (d). In table 2 the number of residual ammonium ions per unit cell (and the corresponding number of protons) is given; they were determined quantitatively by heating the samples to 1100 K, absorption of the desorbed ammonia in 0.1 N sulfuric acid and titration with alkali.

The relative amount of amorphous parts contained in the zeolite samples was determined by X-ray diffraction intensity measurements of characteristic lines and a comparison with reference samples. Some results are collected in table 3.

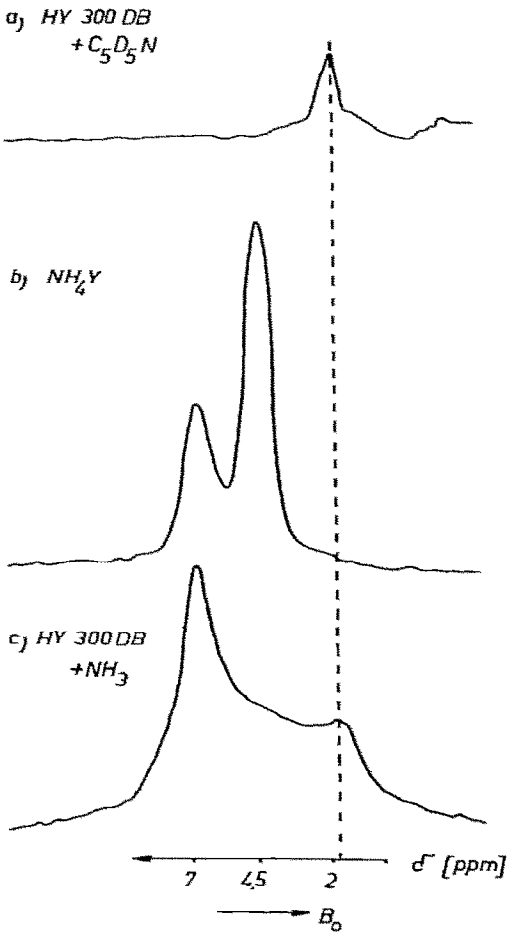

Fig. 2. MAS proton magnetic resonance spectra of HY and NH_4Y zeolites. (a) HY 300 DB, loaded with ≈45 C_5D_5N molecules per unit cell, 270 MHz; (b) NH_4Y, 90 MHz; (c): HY 300 DB loaded with ≈25 NH_3 molecules per unit cell, 90 MHz.

Table 2
Number $n_{NH_4^+}$ of residual ammonium ions (and n_H for the corresponding number of protons) per unit cell of HY zeolites determined by thermodesorption up to 1100 K

Zeolite	$n_{NH_4^+}$	n_H
300 SB	0.72 ± 0.04	2.88 ± 0.16
400 SB	0.16 ± 0.02	0.64 ± 0.08
300 DB	2.26 ± 0.12	9.04 ± 0.48
400 DB	1.4 ± 0.08	5.6 ± 0.32

Table 3
Relative amount of amorphous parts p_a contained in NaY, NH_4Y and HY zeolites

Sample	p_a (%)	
NaY	100	reference substances
amorphous silica-alumina	0	reference substances
NH_4Y –	100 ± 3	
HY 300 DB	90 ± 3	
HY 400 DB	80 ± 3	
HY 500 DB	80 ± 3	

4. Discussion

(a) The signal at 1.8 ppm. As shown in former work [4,5], the non-acid OH groups of silica gel and γ-Al_2O_3 give rise to proton magnetic resonance signals characterized by resonance shifts of about 1.8 ppm. A loading of the zeolite samples with ammonia or pyridine cannot annihilate these signals (figs. 2c and 2a). That means that the protons of these OH groups are not involved in the protonation of ammonia or pyridine. Uytterhoeven et al. [16] have shown that a 1 μm zeolite crystal requires about 0.25 OH groups per unit cell to terminate the crystal faces. The values for the intensity of line (a) collected in table 1 are, however, one order of magnitude greater and we conclude that a large number of OH groups formed at lattice defects contribute to this signal. The experimentally observed broadening of line (a) with increasing activation temperature (400 Hz and 800 Hz for 300 SB and 500 DB, respectively) can be explained by hydroxyl groups formed at extra-lattice aluminium [17], since these exhibit greater linewidths than silicon OH groups.

(b), (c) The signals at 3.9–4.6 and 4.8–5.6 ppm. The vanishing of both lines on addition of ammonia or pyridine (figs. 2a and 2c) proves that these OH groups are acid, a behaviour which is ascribed to so-called structural hydroxyl groups formed in zeolites at O_1 and O_3 types of oxygen [18]. Due to proton exchange [11] and as a consequence of the much longer time scale of NMR measurements, both lines, and not only the signal of O_1H groups, as in infrared spectroscopy (the so-called high-frequency band) [2], are influenced. Assuming that the structural hydroxyl groups can exist only in the neighbourhood of lattice aluminium, the number of protons contributing to lines (b) and (c) must be equal to the number of those aluminium nuclei which give rise to an ^{27}Al NMR signal with a resonance shift characteristic of four-fold coordinated aluminium. This fact was proved in an earlier paper [6] where, however, the resolution was not sufficient to separate lines (b) and (c).

(d) The signal at 7.0–7.5 ppm. As can be seen by comparison of the last columns of tables 1 and 2, the signal at 7.0–7.5 ppm may be explained roughly by residual ammonium ions. At present however, it cannot be excluded that a few protons exist (less than about 3–5 per unit cell) which additionally contribute to this signal. In this respect it is of importance that acid protons in amorphous silica-alumina give rise to a line at about 7 ppm [5]. Work is in progress to study in more detail whether these protons are due to structural OH groups of the amorphous parts contained in the zeolite samples (cf. table 3 and ref. [5]).

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