Magic-angle-spinning nuclear magnetic resonance and infrared studies on modified zeolites

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Abstract

$^{11}$B MAS NMR yields quantitative information about the incorporation of boron into zeolite frameworks. $^1$H MAS NMR and IR spectroscopy show that OH groups introduced into the framework by boron substitution are non-acidic. 2D proton spin diffusion measurements of the zeolite SAPO-5 reveal that defect OH groups are adjacent to acidic bridging hydroxyl groups and do not exist in an amorphous phase. Strongly adsorbed water molecules in mildly steamed zeolites H-Y can be explained by Lewis sites.

1. INTRODUCTION

The study of zeolite adsorption sites capable of donating protons to or accepting electron pairs from molecules adsorbed on these sites is one of the most important areas in heterogeneous catalysis. In this paper recent results of MAS NMR and infrared studies on modified zeolites will be presented. The application of 2D $^1$H MAS NMR gives new information about the Brønsted and Lewis sites.

2. ZSM-5-TYPE BOROALUMINOZEOLITES

ZSM-5 zeolites can be synthesized without an organic template by hydrothermal synthesis but only with relatively high Al contents ($\text{Si/Al} = 10 - 20$) [1]. We have studied this synthesis with a batch composition

$4 \text{Na}_2\text{O} (1-x)\text{Al}_2\text{O}_3 \times \text{B}_2\text{O}_3 \times \text{ySiO}_2$ with $0 \leq x \leq 0.6, \ 20 \leq y \leq 40$

to determine the coordination state of boron atoms in zeolites. $^{11}$B MAS NMR measurements were generally carried out on rehydrated samples, which were kept in a desiccator for 48 h over aqueous $\text{NH}_4\text{Cl}$. For $^1$H MAS NMR and NIR samples, shallow-bed like activation conditions were utilized in a glass tube of 5.5 mm inner diameter and with 10 mm bed-depth of zeolite. The temperature was increased at a rate of 10 K per h. The samples were kept at the final
activation temperature of 673 or 873 K under a pressure below 10^{-2} Pa for 24 h and then cooled and sealed. A modified BECKMAN photospectrometer and a Bruker MSL 300 NMR spectrometer equipped with a home made MAS probe were used.

As shown in Figure 1, $^{11}$B MAS NMR spectra demonstrate the boron incorporation into the zeolite framework during the synthesis. The narrow line at -3.6 ppm is due to tetrahedrally coordinated framework boron and the broader line at ca. -2.0 ppm is caused by boron atoms in the amorphous part of the sample. For a crystallization time $t_k > 7$ h the boron is completely incorporated into the framework.

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In addition, we have studied the hydrogen form of a zeolite ZSM-5, containing 0.72 boron atoms per unit cell. The results of $^1$H MAS NMR, NIR and $^{11}$B MAS NMR studies are given in Figure 2. Three types of hydroxyl groups can be found in the spectra of boron containing zeolites in the hydrogen form: SiOH groups on the surface of zeolite crystallites and at defect sites giving rise to a signal at $2.0 \pm 0.2$ ppm (line a), SiOHB groups causing a line at $2.5 \pm 0.2$ ppm (line a') and bridging SiOHAl groups giving rise to the signal at ca. $4.0$ ppm (line b). This shows that the SiOHB groups are much less acidic than the bridging hydroxyl groups. Lines a and a' cannot be resolved in Figure 2. The chemical shift of the centre of gravity of the overlapping signals

![Figure 1. $^{11}$B MAS NMR spectra of boroaluminozeolites for various crystallization times $t_k$. C denotes the crystallinity of the sample determined by X-ray diffraction and F is the fraction of boron incorporated into the framework which is determined by $^{11}$B MAS NMR.](image)
(2.3 ppm in Figure 2A) increases with the concentration of boron in the framework. The concentration of SiOH groups is independent of the boron content. Concerning the concentration of Brönsted sites we found that for the hydrogen form of the zeolites, the number of bridging hydroxyl groups is in good agreement with the number of framework aluminium atoms determined by $^{27}\text{Al} \text{MAS NMR}$ of the hydrated samples.

The NIR spectrum in the OH combination vibration region shows two peaks: the band due to bridging OH groups at $4655 \pm 10$ cm$^{-1}$ and the band of the non-acidic SiOH groups at $4545 \pm 10$ cm$^{-1}$. The signal of the SiOH groups is (as in the $^1\text{H} \text{MAS NMR}$ spectra) superimposed on the signal of the SiOH groups. An additional band appears at $4385 \pm 50$ cm$^{-1}$ due to non-acidic AlOH groups.

The $^{11}\text{B} \text{MAS NMR}$ spectrum of the hydrated sample shows one line at $-3.3 \pm 0.1$ ppm which is assigned to boron atoms incorporated into the zeolite framework. Other samples which are not completely crystalline contain boron in the amorphous part, giving rise to a broad line at about $-2.0$ ppm. Therefore, the intensity of the line at $-3.3$ ppm may be used to determine the concentration of framework boron atoms.

3. SAPO-ZEOLITES

The preparation and measurement of the samples SAPO-5 and SAPO-11 [2-3] were carried out in the same way as described above. The spectra of $^1\text{H} \text{MAS NMR}$ and NIR measurements are shown in Figures 3 and 4. Four lines or bands of OH groups appear: Two NMR signals (line b at 3.9 ppm and line c at 4.9 ppm) and two bands in NIR (4677 cm$^{-1}$ and 4608 cm$^{-1}$) are caused by OH groups with and without interaction with lattice oxygens, respectively. The line at 2.1 ppm (line a) is connected with SiOH and possibly with POH groups. The band at 4380 cm$^{-1}$ due to non-acidic AlOH groups corresponds to a signal at about 3 ppm, which could not be resolved in the $^1\text{H} \text{MAS NMR}$ spectrum.
The 2D proton spin diffusion spectrum (NOESY experiment [5]) in Figure 5 shows cross peaks due to lines a and b, hydroxyl groups at defect sites and bridging OH groups, respectively. These cross peaks are caused by spin diffusion during the mixing period of 50 ms. Since line b is caused by bridging hydroxyl groups in the main channels of the SAPO-5 framework, the adjacent defect OH groups which are included in the spin exchange process must be located in these channels.

Figure 3. $\textsuperscript{1}H$ MAS NMR (A) and NIR (B) spectra of SAPO-5 pretreated at 673 K.

Figure 4. NMR (A) and NIR (B) spectra of SAPO-11, pretreated at 873 K.

Figure 5. Contour plot of the 2D spin diffusion spectrum of the hydroxyl protons of SAPO-5. $S(t_1, t_2)$ has been recorded with a $\pi/2-t_1-\pi/2-t_M-\pi/2-t_2$ experiment, a mixing period of $\tau_M=50$ ms and a MAS frequency of 5 kHz. Asterisks denote cross peaks of lines a and b.
4. DEALUMINATED ZEOLITES H-Y

The ammonium form of the Y zeolite was prepared by an 88±3% cation exchange in an aqueous solution of ammonium nitrate starting from Na-Y (Zeosorb Y, Chemie AG Bitterfeld-Wolfen, Si/Al=2.6). The hydrothermal treatment was carried out in a tube of 5 mm inner diameter with 8 mm maximum bed depth containing ca. 2 g of the zeolite H-Y. At first, the temperature was increased up to 810 K at a rate of 10 K min⁻¹ in a water-free nitrogen stream of 1 dm³ min⁻¹. Finally, the sample was steamed at this temperature for 20 h under a vapour pressure of 4 kPa, adjusted by the temperature of the water bath through which the nitrogen was flowing.

For the ¹H MAS NMR measurements all samples were pretreated as described above at 673 K. Before being sealed, the samples were loaded at room temperature under vacuum with doubly distilled water.

A pulse length of 4 µs for the π/2 pulse, a recycle delay of 10 s and a rotational frequency of 2500±5 Hz were used for the ¹H MAS NMR and 2D experiments. The ²⁷Al NMR pulse length of 1 µs corresponds to a π/12 pulse for non-selective excitation.

![Figure 6. ¹H MAS NMR spectra of the hydrothermally dealuminated zeolite (DeY), activated under 670 SB conditions: unloaded (A), rehydrated with up to 10 H₂O per unit cell (B) and (C), ca. 40 H₂O per unit cell (D) and after full (ca. 240 H₂O per unit cell) rehydration (E), and ²⁷Al NMR and ²⁷Al MAS NMR spectra of samples (D) and (E); (F) and (G), respectively. Asterisks denote MAS sidebands.](image)
Figure 6 shows $^1$H MAS NMR spectra of the hydrothermally dealuminated zeolite H-Y (DeY) with a framework Si/Al ratio of 5.0±0.5. The spectrum of the dehydrated sample (Figure 6A) consists of two signals, a peak at 1.8±0.2 ppm due to 17±3 silanol groups per unit cell, on the external surface of the crystallites and at crystal defects (line a), and a shoulder at 4.0±0.2 ppm due to 5.6±1.5 bridging OH groups per unit cell (line b). As shown in Figure 6B, after the adsorption of water, a line at 6.5±0.2 ppm appears, not shifted in frequency up to a loading of 10 H$_2$O per unit cell (Figure 6C). The maximum concentration of water molecules giving rise to this line is 2 H$_2$O per unit cell. The shoulder due to bridging OH groups is not affected by a small loading (Figure 6B). With a higher loading a broad line appears at ca. 4 ppm which is caused by physically adsorbed water molecules (Figure 6D).

In Figures 7 and 8 the 2D proton exchange spectrum of the hydrothermally dealuminated zeolite H-Y loaded with ca. 40 H$_2$O per unit cell (identical to the sample in Figure 6C) is shown as contour and stacked plot, respectively. A homonuclear 2D ROESY pulse sequence [5] and a spin lock pulse of 2 ms were used. The absence of cross peaks between the signals at 1.8±0.2 ppm and 6.5±0.2 ppm shows that there is no chemical exchange in the time scale of one millisecond and that the latter signal is caused by protons of strongly adsorbed water molecules probably located at Lewis sites [4].

![Figure 7. Contour plot of the 2D proton exchange spectrum of the hydrothermally dealuminated zeolite H-Y loaded with ca. 40 H$_2$O.](image)
5. ACKNOWLEDGEMENT

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6. REFERENCES