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Multinuclear solid-state n.m.r. investigation of zeolite MCM-22

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In this paper, the results of the first high-field (B_0 = 17.6 T) ^{27}Al MAS n.m.r. measurement on zeolite MCM-22 are reported. The ^{29}Si and ^{27}Al MAS n.m.r. spectra of as-synthesized and dealuminated zeolite MCM-22 were interpreted by signals of framework silicon and aluminum atoms located on at least five crystallographically nonequivalent T sites. After ammonium exchange and calcination of zeolite MCM-22, acidic bridging OH groups identified by a ^{1}H MAS n.m.r. signal at 4.2 ppm are formed. Using ^{29}Si CP/MAS n.m.r. spectroscopy these bridging OH groups were attributed to hydroxyl protons bonded via oxygen bridges to Si(1 Al) atoms located on all the at least five crystallographically nonequivalent T sites.

Keywords: MCM-22; crystallographically nonequivalent T sites; solid-state n.m.r.; high-field ^{27}Al MAS n.m.r.

INTRODUCTION

Zeolite H-MCM-22 has been claimed in the patent literature to be a useful catalyst for a variety of acid-catalyzed reactions, such as isoalkane/olefin alkylation,[1] skeletal and double-bond isomerization of olefins,[2] and the conversion of methanol or olefins to higher hydrocarbons.[3] A model for the structure of zeolite MCM-22 was proposed very recently by Leonowicz et al.[4] In brief, it contains large supercages (ca. 0.71 × 0.71 × 1.82 nm) which are accessible via 10-membered ring windows, and an independent second channel system of two-dimensional, sinusoidal channels with 10-membered ring openings. In agreement with this model it has been concluded from a Spaciousness Index of 8 that the effective pore size of MCM-22 is in the intermediate region between those of 10-membered ring zeolites and very open 12-membered ring structures.[5] Recent studies have demonstrated that solid-state n.m.r. spectroscopy is a powerful method for characterizing the local structure of zeolites,[6,7] e.g., the mean T–O–T angles of crystallographically nonequivalent T sites and the populations of these framework sites. Furthermore, ^{1}H MAS n.m.r. spectroscopy allows a quantitative study of Brönsted sites in acidic zeolites.[8,9] Here we present results of a detailed characterization of zeolite MCM-22 and dealuminated MCM-22 using n.m.r. spectroscopy.

EXPERIMENTAL

Zeolite MCM-22 was synthesized as described recently[5] using hexamethyleneimine as organic template. A gel of the molar composition 32.2 SiO_2/Al_2O_3/2.7 Na_2O/10.6 hexamethyleneimin 1333 H_2O/0.22 H_2SO_4 was autoclaved for 12 days at 423 K under continuous agitation. To remove the template molecules the as-synthesized material was calcined for 48 h at 810 K in a purge of nitrogen gas containing 5 vol% oxygen (parent sample, denoted MCM-22/p). The ammonium form was prepared by 4-fold ion-exchange at 350 K for 12 h in a surplus of a 1 N aqueous solution of NH_4NO_3. Calcination of the samples was performed under vacuum with a heating rate of 10 K/h. At the final temperature of 673 K, the samples were kept for 20 h in a vacuum of 0.01 Pa (product denoted MCM-22/H1). Volumetrically controlled adsorption of ammonia was carried out on MCM-22/H1.

The parent zeolite MCM-22/p was dealuminated according to the method of Beyer and Belenykaja[10] using $SiCl_4$ vapor at 620 K (product denoted MCM-22/deal). From the bulk chemical analysis using atomic emission spectroscopy with inductively coupled plasma (AES/ICP), n_{Si}/n_{Al} ratios of 11 and 20 were determined for the zeolites MCM-22/p and MCM-22/deal, respectively. Zeolite MCM-22/deal was again exchanged with ammonium ions and calcined in vacuum as described above (product denoted MCM-22/H2).

The ^{29}Si and ^{1}H MAS n.m.r. studies were carried out on a Bruker MSL 400 spectrometer at resonance frequencies of 79.5 and 400.1 MHz, respectively. The ^{27}Al n.m.r. measurements were performed in part on the same Bruker MSL 400 spectrometer at the resonance frequency of ν_{L1} = 104.2 MHz and in part on a Bruker AMX 750 spectrometer at ν_{L2} = 195.4 MHz. The pulse lengths were adjusted to $\pi/4$ for ^{1}H and ^{29}Si n.m.r. and to $\pi/12$ for ^{27}Al n.m.r. The ^{29}Si CP/MAS n.m.r. spectra were recorded with a contact time of 2.5 ms. The chemical shifts are referenced to

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the following external standards: tetramethylsilane for ^{1}H and ^{29}Si MAS n.m.r. and a 0.3 N aqueous solution of $Al(NO_3)_3$ for ^{27}Al MAS n.m.r. spectroscopy.

RESULTS AND DISCUSSION

^{29}Si MAS n.m.r. spectroscopy

The ^{29}Si MAS n.m.r. spectra of the parent zeolite MCM-22/p (n_{Si}/n_{Al} = 11) and the dealuminated zeolite MCM-22/deal (n_{Si}/n_{Al} = 20) are presented in *Figure 1, a* and *b,* respectively. Because of the relatively low aluminum content of the dealuminated sample, its ^{29}Si MAS n.m.r. spectrum consists mainly of lines originating from silicon atoms connected with four silicon atoms in the first coordination sphere of T atoms (Si(0Al)).[11] Therefore, the peaks in the spectrum of the dealuminated zeolite (MCM-22/deal) in *Figure 1b* can be attributed to five Si(0Al) lines appearing at chemical shifts of −118.5, −115.3, −112.3, −110.3, and −104.0 ppm (accuracy ± 0.2 ppm). For a zeolite with a higher aluminum content, a corresponding set of signals due to Si(1Al) should appear, which is shifted to lower field strengths by about 5–6 ppm.[12] In agreement with this assumption, an Si(1Al) signal at −98.0 ppm can be observed in the ^{29}Si MAS n.m.r. spectrum of zeolite MCM-22/p (*Figure 1a*). The intensity of this signal is reduced upon dealumination (cf. *Figure 1b*). Considering these facts, the ^{29}Si MAS n.m.r. spectra in *Figures 1, a* and *b,* were simulated by two sets of five lines: five lines for Si(0Al) and five lines for Si(1Al) atoms. Since only a small amount of extraframework aluminum was detected by ^{27}Al MAS n.m.r. (see below) the simulation was carried out with relative intensities of the two sets of Si(1Al) and Si(0Al) lines of 1:1.75 for zeolite MCM-22/p and 1:4 for zeolite MCM-22/deal. These intensity ratios were calculated from the number of aluminum atoms determined by AES/ICP. The simulations of the ^{29}Si MAS n.m.r. spectra in *Figures 1, a* and *b,* yield the following resonance positions for the five Si(1Al) lines: −112.5, −110.5, −107.5, −104.5, and −98.0 ppm (accuracy ± 0.5 ppm). In addition, the simulation of the spectrum of zeolite MCM-22/p (*Figure 1a*) requires the assumption of a line at −102 ppm with a relative intensity of about 5%. This signal is supposed to originate from silanol groups at framework defect sites and/or on the external surface of crystals.[13,14] For the dealuminated sample, a satisfactory fitting of the experimentally recorded spectrum was achieved already without assuming a signal at −102 ppm. This could indicate the healing of framework defects during the $SiCl_4$ treatment. To detect the location of hydroxyl groups, the ^{29}Si MAS n.m.r. spectrum of dehydrated zeolite MCM-22/H1 was recorded by applying cross-polarization (CP). The simulation of the experimentally recorded ^{29}Si CP/MAS n.m.r. spectrum (cf. *Figure 1c*) requires at least six signals: five Si(1Al) lines at the resonance positions of −113.0, −110.5, −108.0, −104.5, and −97.0 ppm (accuracy ± 0.5 ppm) and one line at −102 ppm,

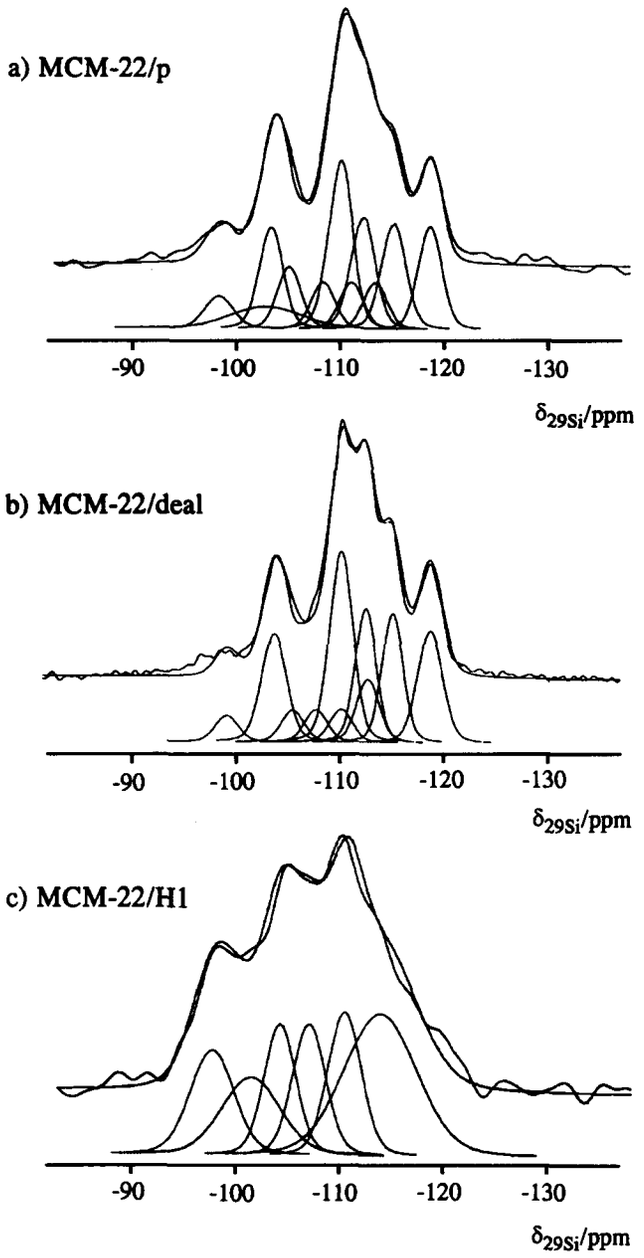


Figure 1 ^{29}Si MAS n.m.r. spectra of (a) hydrated zeolite MCM-22/p, (b) dealuminated zeolite MCM-22/deal, and (c) zeolite MCM-22/H1 calcined at 673 K. Spectrum (c) was recorded with cross-polarization and a contact time of 2.5 ms (number of scans 45,000). The single components used for simulation are depicted on the bottom; the superposition of the simulated and the experimentally recorded spectrum are shown on the top.

originating from silanol groups. This result demonstrates that in the acidic form of zeolite MCM-22, hydroxyl protons of briding OH groups are bonded via oxygen bridges to Si(1Al) atoms located on all five crystallographically nonequivalent T sites.

The simulation of the ^{29}Si MAS n.m.r. spectra presented in *Figure 1, a* and *b,* results in relative intensities for the five Si(0Al) signals from high field to low field corresponding to 2:2:2:3:2 (accuracy ± 20%). Because of the limited resolution of the spectra we cannot exclude a superposition of the ^{29}Si MAS

n.m.r. signals of additional crystallographically nonequivalent T sites at the above-mentioned resonance positions of the experimentally observed Si(0Al) lines. However, the spectra indicate that zeolite MCM-22 is built up by silicon atoms located on at least five crystallographically nonequivalent positions. Using the correlations published recently by Fyfe and coworkers[6] mean Si–O–T angles between 133 ± 4° and 164 ± 4° can be estimated from the chemical shifts of the Si(0Al) lines. The structural model proposed recently[4] contains eight crystallographically nonequivalent T sites with T–O–T angles in the range from 136 to 164°. Hence the n.m.r. data support this model.

^{27}Al MAS n.m.r. spectroscopy

Figure 2 shows the ^{27}Al MAS n.m.r. spectra of zeolites MCM-22/p (*a* and *c*) and MCM-22/deal (*b* and *d*) recorded at the resonance frequencies of ν_{L1} = 104.2 MHz and ν_{L2} = 195.4 MHz, respectively. The amplitudes of the spectra in *Figure 2, b* and *d*, are increased by a factor of about 2 with respect to those of the spectra in *Figure 2, a* and *c*, to account for the lower concentration of aluminum atoms in the dealuminated sample. Although the spectrum of zeolite MCM-22/p shows no signal of extraframework aluminum, such a line does appear at 0 ppm with a relative intensity of about 5% in the spectrum of zeolite MCM-22/deal (not shown in *Figure 2*). In agreement with the spectra recorded at the resonance frequency of ν_{L1} (*Figure 2, a* and *b*), the spectra recorded at ν_{L2} (*Figure 2, c* and *d*) show peaks at about 49 and 57 ppm and a low-field shoulder. Since the resonance positions of the peaks and of the center of gravity do not depend on the applied magnetic field strength, the quadrupolar interactions of the corresponding tetrahedrally coordinated framework aluminum atoms can be neglected, hence the MAS n.m.r. line shapes were fitted by Gaussian curves. MAS n.m.r. studies performed by Jacobsen et al.[12] on aluminosilicate sodalites yielded a linear correlationship between the ^{27}Al and ^{29}Si chemical shifts of framework atoms. Assuming an analogous correlation for the resonance positions of framework silicon and aluminum atoms in zeolite MCM-22, five Gaussian curves in the range of chemical shifts between 50 and 60 ppm were used

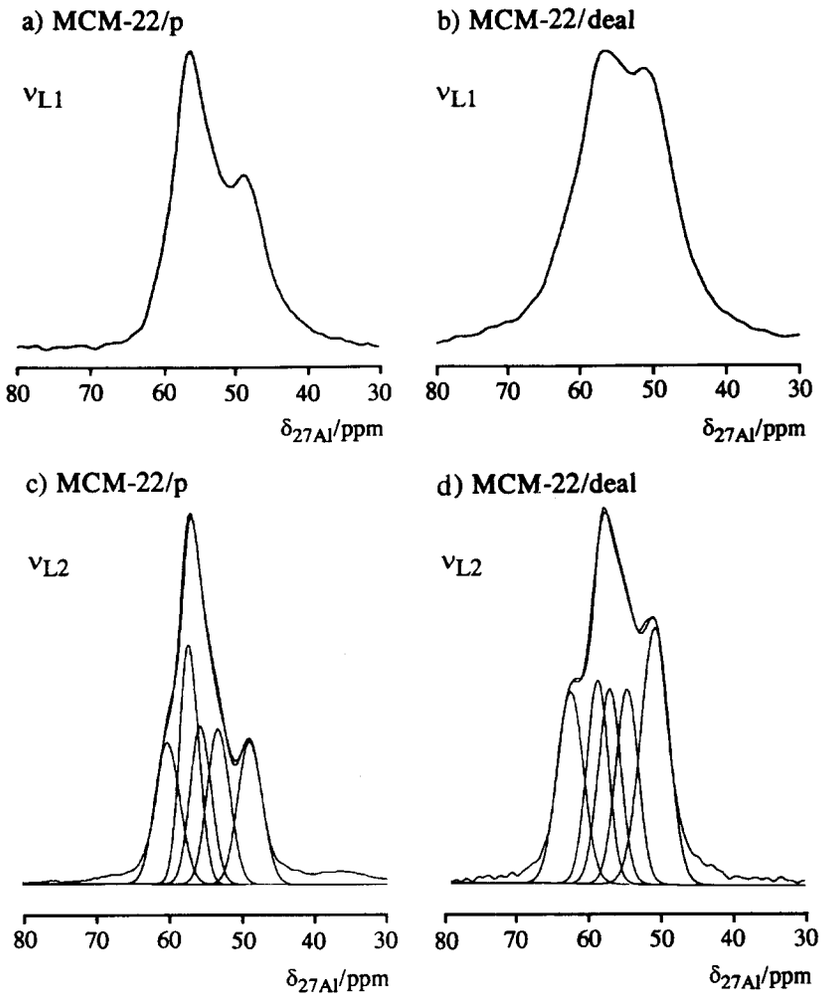


Figure 2 ^{27}Al MAS n.m.r. spectra of hydrated zeolites MCM-22/p (a, c) and MCM-22/deal (b, d) recorded at a resonance frequency of ν_{L1} = 104.2 MHz (a, b) and ν_{L2} = 195.4 MHz (c, d). In (c) and (d) the fits of the experimentally recorded and the simulated spectra as well as the single components used for simulation are shown.

to simulate the ^{27}Al MAS n.m.r. spectra given in *Figures 2, c* and *d*. In agreement with this procedure, no satisfactory fitting of the spectra recorded at ν_{L2} was achieved assuming less than five signals. The best matching between the experimentally recorded and the simulated spectra was achieved with line positions at chemical shifts of 49.0, 53.5, 55.5, 57.5, and 62.0 ppm (*Figure 2, c* and *d*). In the ^{27}Al MAS n.m.r. spectrum of zeolite MCM-22/p these lines have an intensity ratio of about 3:3:3:4:3 (accuracy ± 0.2) from high field to low field. After dealumination of zeolite MCM-22/p the intensities of all lines decrease to approximately the same value, except the high-field signal at 49 ppm (*Figure 2d*), which corresponds in this sample to the framework T site with the highest aluminum population.

^{1}H MAS n.m.r. spectroscopy

The ^{1}H MAS n.m.r. spectrum of the calcined zeolite MCM-22/H1 (*Figure 3a*) consists of signals at 1.9, 2.8, 4.2 (accuracy ± 0.1 ppm), and a broad hump at 6.2 ppm (accuracy ± 0.5 ppm). The lines at 1.9 and 2.8 ppm have been attributed to silanol groups at framework defects and OH groups at extraframework aluminum species,[8,9] respectively. In agreement with previous studies[8,9] the signal appearing at 4.2 ppm is assigned to acidic bridging OH groups and the broad hump at about 6.2 ppm to residual ammonium ions. Upon adsorption of ammonia on the calcined sample under vacuum, the line at 4.2 ppm disappears, and the signal of ammonium ions at about 6.8 ppm can be observed (*Figure 3b*). The complete disappearance of the signal of bridging OH groups indicates that the number of adsorbed ammonia molecules is equal to the number of bridging OH groups. By this method, the density of acidic bridging OH groups ($n_{OH}/m_{zeolite}$) was determined to (7.8 ± 0.8) × 10^{20} g^{-1}. Using the ^{1}H MAS n.m.r. line at 6.8 ppm of the reammoniated sample (*Figure 3b*) as internal intensity standard, the density of silanol OH groups can be estimated to (5.6 ± 0.6) × 10^{20} g^{-1}. As expected, the dealumination of zeolite MCM-22/p by $SiCl_4$ is coupled with a strong decrease in the density of bridging OH groups at the chemical shift of 4.2 ppm to (2.6 ± 0.3) × 10^{20} g^{-1} (*Figure 3c*). It is interesting to note that the density of silanol groups is decreased by a factor 2 as well. The reduced line width of the SiOH signal and the splitting into two components is caused by a decrease in the dipolar proton-proton interaction. The two SiOH components at 1.8 and 2.1 ppm may be explained by terminal OH groups at the external surface and by internal silanol groups at open Si–O–Si linkages,[15] respectively.

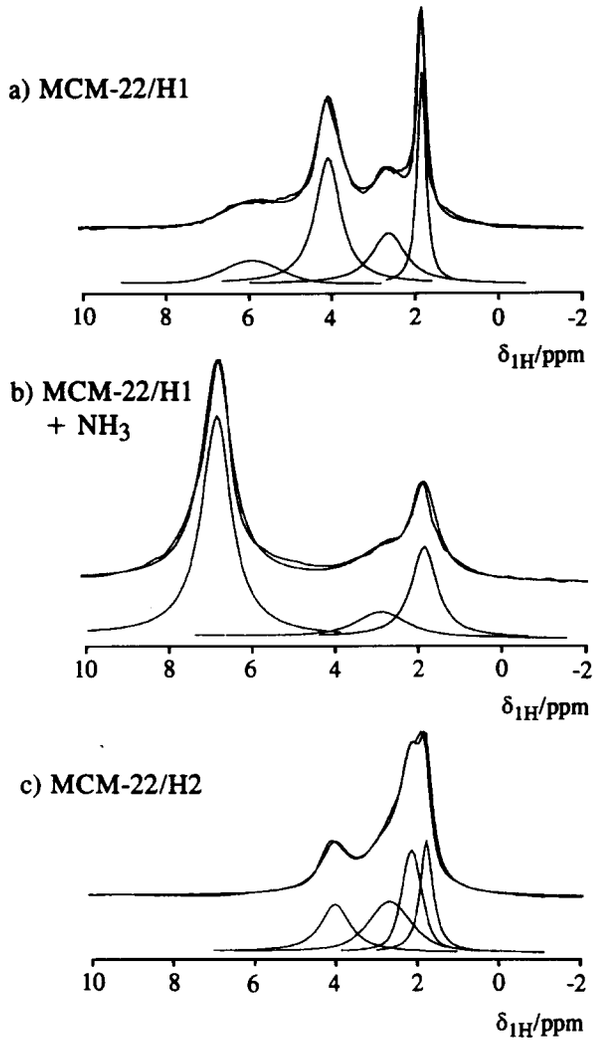


Figure 3 ^{1}H MAS n.m.r. spectra of dehydrated (673 K) zeolites MCM-22/H1 (a) and MCM-22/H2 (c) and after adsorption of 7.8 × 10^{20} molecules of NH_3/g of dry zeolite MCM-22/H1 (b) (ν_{rot} = 10 kHz). The single components used for simulation are depicted on the bottom; the superposition of the simulated and the experimentally recorded spectrum are shown on the top.

CONCLUSION

The ^{29}Si and ^{27}Al MAS n.m.r. spectra of zeolite MCM-22 were interpreted by signals of framework silicon and aluminum atoms occupying at least five crystallographically nonequivalent T sites of the MCM-22 structure. The mean Si–O–T angles of the corresponding T sites were estimated to be in the range between 133 ± 4 and 164 ± 4°. Both the minimum number of crystallographically nonequivalent T sites and the mean Si–O–T angles as derived from solid-state n.m.r. spectroscopy do confirm the proposed structural model of zeolite MCM-22.[4] It is important to note that because of the limited resolution, a superposition of the signals of additional crystallographically nonequivalent T sites in the observed ^{29}Si and ^{27}Al MAS n.m.r. lines cannot be excluded. Dealumination of zeolite MCM-22 by $SiCl_4$ was found to decrease the aluminum population of all T positions approximately to the same extent, except the crystallographic position corresponding to the high-field ^{27}Al MAS n.m.r. line at 49 ppm. This crystallographic T site has the highest aluminum population in dealu-

minated zeolite MCM-22, at complete variance to the parent zeolite.

In the ^{1}H MAS n.m.r. spectra of ammonium-exchanged and calcined MCM-22 zeolites, acidic bridging OH groups were observed at a chemical shift of 4.2 ppm. Hence, there is a reasonable agreement with values of the chemical shift determined for bridging OH groups in zeolites H-ZSM-5 and H-mordenite with framework n_{Si}/n_{Al} ratios ≥ 10.[8,9] The amount of 7.8×10^{20} acidic bridging OH groups/per g of dry zeolite MCM-22/H1 agrees well with the density of 8.4×10^{20} aluminum atoms/g of dry zeolite determined by AES/ICP. The large density (5.6×10^{20} g^{-1}) of silanol groups in the as-synthesized zeolite MCM-22/p is a hint for a corresponding number of internal framework defects caused by open Si–O–Si linkages.

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