Aluminium Coordinations in Zeolite Mordenite By ^{27}Al Multiple Quantum MAS NMR Spectroscopy

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^{27}Al 3Q MAS NMR spectroscopy has been applied to study the coordination state of the species giving the 30 ppm Al NMR signal in the ^{27}Al MAS NMR spectrum of activated mordenite materials. From the ^{27}Al 3Q MAS NMR measurements it is evident that the broad peak at 30 ppm in the ^{27}Al NMR spectrum of the mordenite calcined at temperatures up to 600 °C comes mainly from the distorted four-coordinated Al. By simulation a quadrupolar coupling constant of 5.8 MHz was estimated for the distorted tetrahedral Al. For samples calcined at 650 and 700 °C, a small amount of pentacoordinated Al emerges. The majority of the signal, however, arises from distorted tetrahedral Al. A two-step calcination results in a significant contribution of the pentacoordinated Al to the signal at 30 ppm. From the simulated line-shape, a quadrupole coupling constant of 6.2 MHz is obtained for the latter signal. These data show that during the calcination of the mordenite, the coordination environment at the Al centre gradually becomes distorted to give rise to the shoulder at 30 ppm. With the increase of the calcination temperature, pentacoordinated Al species form

Introduction

Since the discovery of the ultrastabilisation process of zeolites, the relationship between the structure and the properties of these materials has puzzled many scientists. ^{27}Al and ^{29}Si solid-state NMR spectroscopy has significantly contributed to unraveling the structural changes accompanying the ultrastabilisation.[1] Although ^{27}Al MAS NMR is nowadays routinely applied in this field of research,[2][3] some questions regarding the interpretation of the spectra still need to be answered due to the interaction of the quadrupolar aluminium nucleus with the surrounding electric field. This not only broadens the spectral lines but also results in a quadrupole-induced chemical shift of the NMR signals.[4]

In the ^{27}Al MAS NMR spectrum of hydrothermally activated zeolites, signals centred at 60, 30 and 0 ppm can easily be observed. The signal at 60 ppm is attributed to tetrahedrally coordinated Al species whereas that at 0 ppm is assigned to octahedrally coordinated species. The interpretation of the signal at 30 ppm, however, needs further discussion. In literature reports on the ultrastable Y zeolite (USY) several assignments are reported for the latter signal: four-coordinated Al species shifted upfield due to the quadrupolar induced chemical shift,[5][6] pentacoordinated Al[7][8] or an overlap of both four- and five-coordinated Al species.[9]

The activation conditions cannot be overlooked in any discussion about the coordination number of the different aluminium species in the activated zeolites. Several studies indicate key differences in the Al speciation due to the method of activation.[5,6,9] Owing to the ability to average out the second-order quadrupolar interaction of the Al nucleus, some improvement regarding the assignment of the signal at 30 ppm was obtained by the technique of Double Rotation (DOR) NMR spectroscopy.[10] In a sample of single thermally treated zeolite Y a signal was observed at 47.5 ppm due to tetrahedrally coordinated Al, while in the doubly hydrothermally treated sample, the signal at 30 ppm was assigned to the pentacoordinated Al species. However, because of the low spinning rates of the inner rotor, spinning side bands can overlap with actual resonance lines.[11] Some ambiguity therefore remains in the assignments.

With the development of two-dimensional multiple quantum MAS NMR spectroscopy a powerful tool for the study of quadrupolar nuclei is available.[12][13] This method can refocus the second-order anisotropic broadening of the half-integer quadrupolar nuclei by selecting the multiple-quantum transition (3Q or 5Q) and transferring it to the single-quantum signal over two time domains. Isotropic resolution can be obtained, while problems with overlapping spinning side bands are avoided because of the high spinning rate of the MAS rotor.

Here we report ^{27}Al 3Q MAS NMR spectroscopic experiments on the activated zeolite mordenite, for which a signal at 30 ppm in the ^{27}Al MAS NMR spectrum has been reported.[14] The focus of this paper will be on the coordination state of the Al species giving rise to this signal.

Results and Discussion

Figure 1 shows the ^{27}Al MAS NMR spectra of the parent and the 550 to 700°C calcined H-mordenite samples after hydration, as well as the two-step activated mordenite. The signal at 55 ppm in the spectrum of parent H-mordenite (Figure 1a) is assigned to the framework tetrahedrally coordinated Al atoms, while that at 0 ppm results from extra-framework Al atoms in an octahedral environment.[14]

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Some framework-related octahedrally coordinated Al may appear at 0 ppm as was recently reported for the HY.[15] The small signal that can be seen at 30 ppm is probably due to activation at 400 °C and the subsequent acid washing that was performed to prepare the acid form of the sample (Figure 1).

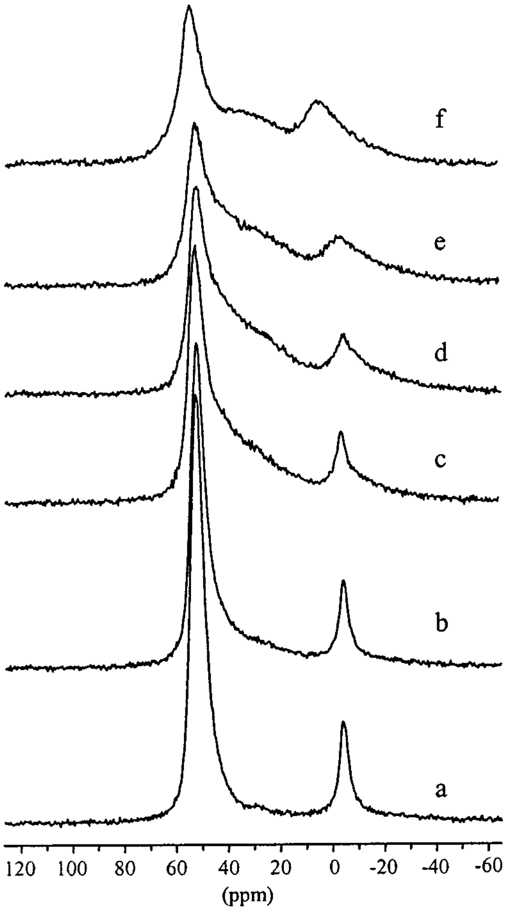

Figure 1. ^{27}Al MAS NMR spectra of zeolite mordenite; (a) parent mordenite, (b) 550 °C calcined, (c) 600 °C calcined, (d) 650 °C calcined, (e) 700 °C calcined and (f) the two-step calcination

In the spectra of the calcined samples (Figure 1, b−f), besides the peaks at 55 and 0 ppm, a broad line gradually emerges at around 30 ppm, with increasing calcination temperature, while the 0 ppm signal broadens. Furthermore, the total Al intensity within the spectra decreases. For the sample calcined at 700 °C, an intensity loss of 15−20% was found relative to the parent sample. The formation of "NMR-invisible Al" at high calcination temperatures is in agreement with the measurements of Grobet et al. for the zeolite Y.[5] Because of this "NMR-invisible Al", quantification of the Al content from the ^{27}Al MAS NMR spectrum is not possible, in contrast to the statement of Barras et al.[14]

By application of the two-dimensional ^{27}Al 3Q MAS NMR technique the resolution of the ^{27}Al MAS NMR spectra of the calcined mordenite samples is enhanced, as shown in Figure 2. In these spectra the position of the lines in the MAS-dimension corresponds to the conventional ^{27}Al MAS NMR measurements, while isotropic resolution is obtained in the second dimension. In the spectrum of the parent H-mordenite (Figure 2a) a strong signal (A) originating from the framework Al and a signal (B) due to the octahedrally coordinated Al are seen. Furthermore a small signal (C) appears near the four-coordinated Al (signal A). From the projection on the MAS-axis signal C can be correlated with the small signal at 30 ppm in the 1D ^{27}Al MAS NMR spectrum (Figure 1a). Artificial peaks along the isotropic dimension near signal (A) can be observed due to the truncation of the NMR signal in the *t1* time domain (see Experimental Section).

After calcination at 550 °C (Figure 2b), signals A and B are still present, while the intensity of signal C is increased. This process continues until 600 °C (Figure 2c). From its position in the isotropic-dimension of the 3Q MAS NMR spectrum, signal C should also be regarded as arising from four-coordinated aluminium species. Pentacoordinated species are expected to be found between signals A and B. From both the centre of gravity and the tailing of the signal in the MAS-dimension a significantly higher quadrupolar coupling constant (QCC) than that of the tetrahedral signal A is expected.

A slice through signal C, parallel to the MAS-dimension, of the sample calcined at 600 °C is shown in Figure 3a. From the fitting of a theoretically calculated powder pattern to this slice the quadrupole parameters can be obtained.[16] Due to the high dispersion which is typical of zeolite samples,[17] only average values can be obtained for both the chemical shift and the quadrupolar parameters. Several authors have published quadrupolar coupling constants for the signal at 30 ppm in the ^{27}Al MAS NMR spectrum of an activated zeolite Y. Ray and Samoson estimated a QCC of 6.2 MHz for a single thermally dealuminated Y sample.[10] Coster et al. indicate that nonframework Al debris in the USY are consists of two species contributing to the signal in 30 ppm region. The first has an isotropic chemical shift of about 58 ppm and a QCC of 6 MHz, the second an isotropic shift of 40 ppm and a slightly lower QCC.[17] For the simulated powder pattern of Figure 3b a quadrupolar constant of 5.8 MHz and an asymmetry parameter (η) of 0.4 were used. These values agree well with those reported in the literature. A Gaussian line broadening of 50 Hz was introduced to the theoretical line shape to account for the dispersion of the chemical shift. The dispersion of the quadrupolar parameters was not taken into account and this may explain the rudimentary nature of the fit. The isotropic chemical shift determined by the simulated pattern is at 59 ppm, giving further evidence that signal C originates from four-coordinated Al as expected from the position of this line in the isotropic dimension. From the high quadrupolar coupling constant, and the consequent dispersion in the 2D MQ spectrum, a highly distorted site is expected. The broad band at 30 ppm in the corresponding 1D spectra (Figure 1a−c) arises from this kind of distorted Al species.

If the temperature of calcination is further increased to 650 °C, an additional signal (D) appears in the ^{27}Al 3Q

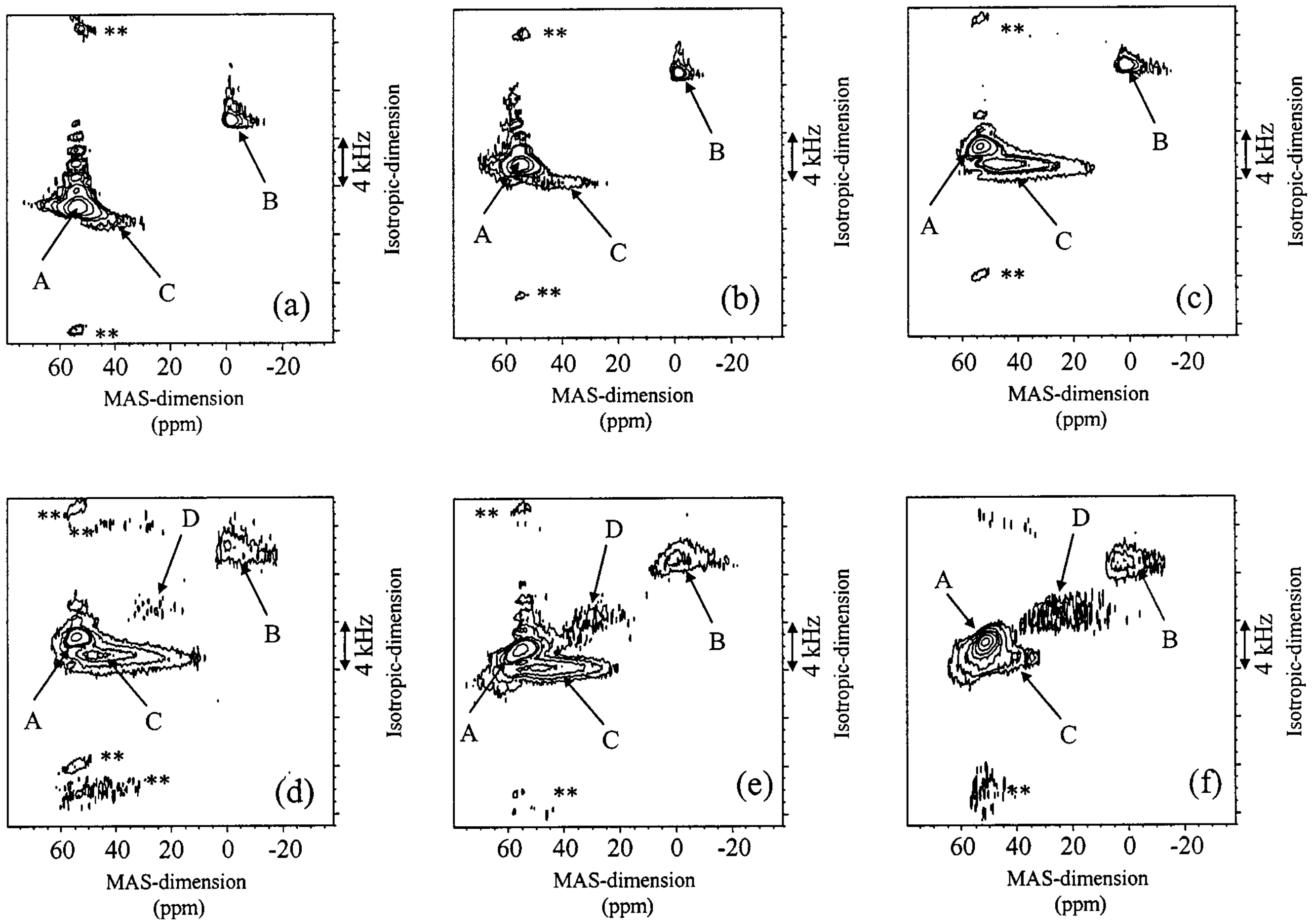

Figure 2. ^{27}Al 3Q MAS NMR spectra of zeolite mordenite; (a) parent sample, (b) 550 °C calcined, (c) 600 °C calcined, (d) 650 °C calcined, (e) 700 °C calcined and (f) the two-step calcination; ** denote spinning side bands

MAS NMR spectrum (Figure 2d). The intensity of signal D is weak but becomes more pronounced after calcination at 700 °C (Figure 2e). The much lower intensity of signal D relative to signal C in Figures 2d and 2e can either be explained by the low quantity of the former species or by differences in the excitation efficiency of the multiple quantum transition under our experimental conditions. From the position of signal D in the ^{27}Al 3Q MAS NMR spectra, which is between those expected for tetrahedral and octahedral coordination, the Al species giving rise to signal D should be pentacoordinated.

From the 3Q MAS NMR spectra it can be observed that signal B gradually broadens in both the MAS and isotropic dimension, implying that its QCC and its isotropic chemical shift became more dispersed. The properties of signal C do not change as the calcination temperature increases from 600 to 700 °C.

Spin-lattice relaxation measurements on the USY revealed that the signal at 30 ppm is not due to a single Al site but results from a mixture of different Al species, which are believed to be in a nonframework environment.[18] From the projection of signals C and D on the MAS-dimension, it is clear that both contribute to the broad hump at 30 ppm in the 1D spectrum.

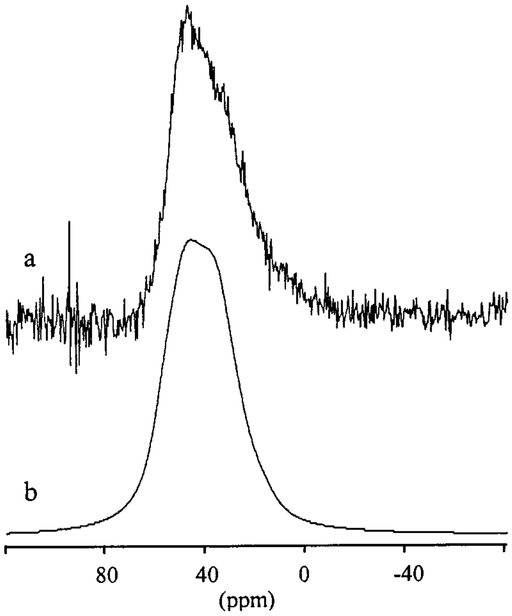

Figure 3. (a) Slice through signal (C) in Figure 2c, (b) simulation with a calculated quadrupolar powder pattern, QCC = 5.8 MHz, $\eta = 0.4$, and $\delta^{cs}{}_{iso} = 59$

After the two-step activation of the mordenite (Figure 2f), a significant contribution of the pentacoordinated Al species (signal D) to the signal at 30 ppm is encountered. By simulation of a slice through signal D, a quadrupolar coupling constant of 6.2 MHz is estimated (Figure 4), which is slightly higher than the value obtained for the distorted tetrahedral Al after a single activation. However, for the two-step calcination of zeolite Y, Ray et al. found a lower QCC for the pentacoordinated Al species than for the distorted Al sites seen after a single hydrothermal treatment.[10] On the other hand, Rocha et al. indicate an increase of the QCC in zeolite Y with increasing degree of dealumination of the sample.[9] These differences may result from the activation conditions applied by the authors.

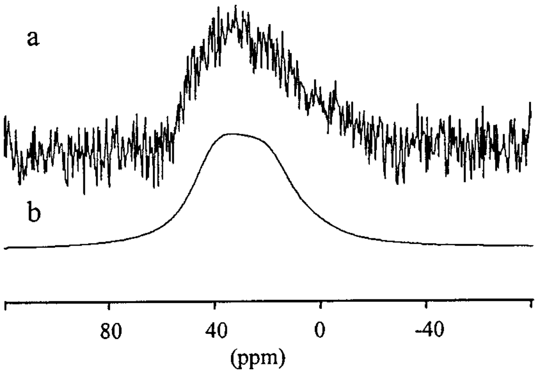

Figure 4. (a) Slice through signal (D) in Figure 2f, (b) simulation with a calculated quadrupolar powder pattern, QCC = 6.2 MHz, $\eta = 0.5$, and $\delta^{cs}_{iso} = 44$

For both the distorted tetrahedral Al sites and the pentacoordinated aluminium similar QCC′s are observed. Therefore the excitation efficiency, which is dependent on the QCC, is not responsible for the low intensity of the pentacoordinated Al species observed in the spectra of samples calcined above 600 °C. This implies that only a small amount of the latter species is formed. The signal at 30 ppm in the ^{27}Al MAS NMR spectrum can thus mainly be assigned to distorted tetrahedral Al. Only after a second activation step does a significant part of this signal result from five-coordinate Al.

Conclusion

In the ^{27}Al MAS spectra of the parent, 550, 600, 650, 700 °C calcined zeolite mordenite, three signals are observed at 55, 30 and 0 ppm, respectively. The 55 ppm signal is related to tetrahedrally coordinated Al species while the 0 ppm line is related to octahedrally coordinated Al. A broad 30 ppm signal gradually appears when the calcination temperature is increased. From the ^{27}Al 3Q MAS NMR experiments it can be concluded that during the calcination of mordenite, tetrahedral Al species gradually undergo distortion. Due to the second order quadrupolar broadening, these species give rise to the 30 ppm shoulder in the 1D spectrum. Further increase of the calcination temperature to 650 °C and above results in the formation of pentacoordinated Al. These species contribute to the 30 ppm signal although the majority of this band remains related to distorted tetrahedral Al. After a second calcination the formation of pentacoordinated aluminium species is more pronounced.

Experimental Section

Samples: Commercially available H-mordenite with a Si/Al ratio of 6.2, referred to as the parent sample, was subjected to different calcination treatments. This parent sample was heated in a muffle furnace for 2 hours at temperatures of 550, 600, 650 and 700 °C. All the calcined samples were placed in a desiccator to hydrate over a saturated NH_4Cl solution for at least one week. After hydration, the sample calcined at 650 °C was calcined a second time at 500 °C for two hours and was subsequently equilibrated in a desiccator. This latter sample will be referred to as the two-step activated mordenite.

NMR Measurements: ^{27}Al NMR spectra were measured on a Bruker MSL-400 spectrometer at 104.26 MHz. The MAS spin rate was 12.5 kHz. ^{27}Al MAS NMR spectra were recorded with a short 0.6 μs pulse (corresponding to $\pi/18$ flip angle). A "split-*t1*" 3Q pulse sequence was applied for the triple-quantum MAS NMR experiments to obtain a sheared spectrum without further treatment of the 2D data.[19] The three pulses of 100 kHz had a length of 3.5, 1.2 and 0.6 μs. 200 FID′s for each experiments were accumulated with a time increment of 5 μs. 1920 scans were accumulated for each FID. The TPPI method was used in the 2D data acquisition and processing. ^{27}Al chemical shifts were referenced to a 0.5 M $Al(NO_3)_3$ solution.

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