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DETERMINATION OF SILICON-ALUMINIUM ORDERINGS IN MORDENITE AND ITS ALUMINIUM DEFICIENT FORMS USING HIGH-RESOLUTION MAGIC-ANGLE-SPINNING ^{29}Si-NMR

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A series of chemically dealuminated mordenites were investigated by ^{29}Si and ^{27}Al NMR spectroscopy. High-resolution magic-angle-spinning (HRMAS) solid state ^{29}Si NMR lines with varying intensity were observed at δ = -95, -105 and -110 ppm. When it is assumed that the Al atoms are located exclusively in the 4-membered rings of the structure, these variations can be explained by assigning the resonance lines to silicon atoms surrounded by 2, 1 and 0 Al atoms respectively. The ^{27}Al NMR spectrum yields quantitative information on the amount of octahedrally coordinated aluminium formed during various chemical treatments of Na-mordenite.

High-resolution magic-angle-spinning ^{29}Si NMR (HRMAS NMR) and, more recently, ^{27}Al HRMAS NMR have added a great deal of understanding to our knowledge on the detailed structure of zeolites. The first technique has been able to resolve crystallographically non-equivalent sites and to throw new light on short-range silicon-aluminium orderings in natural[1,2] and synthetic zeolites such as faujasites[2-6], ZK-4[7,8] and pentasil-type materials.[9-11] ^{27}Al HRMAS NMR was used to discriminate between framework (tetrahedrally coordinated) and extra-framework (octahedrally coordinated) aluminium.[9,12] Finally, these techniques led also to quantitative determination of Si/Al ratios in zeolitic frameworks.

^{29}Si HRMAS NMR spectra of zeolites may contain up to five different lines reflecting the arrangements of corner sharing SiO_4 and AlO_4 tetrahedra. Their assignment to a particular Si (n Al) configuration ($0 \leqslant n \leqslant 4$) can be achieved upon examining their intensity variation as a function of the dealumination treatment of the zeolite.[13,14]

The present paper deals with the assignment of the three lines in the ^{29}Si HRMAS NMR spectrum of mordenite, leading to a detailed model for the silicon-aluminium ordering in the mordenite structure. ^{27}Al NMR was used to determine environmental changes of lattice Al during dealumination treatments and to derive the actual chemical composition of the samples.

The parent Na-mordenite (Na-MOR), a Na-zeolon sample from Norton, was progressively dealuminated by subsequent treatments with nitric acid, as follows :

H-MOR-1 : with 4M HNO_3 at 293 K for 8h
H-MOR-2 : with 4M HNO_3 at 323 K for 24h
H-MOR-3 : with 4M HNO_3 at 363 K for 24h
H-MOR-4 : with 6M HNO_3 at 363 K for 24h
H-MOR-5 : with 14M HNO_3 at 363 K for 24h.

The degree of dealumination was measured by chemical analysis (atomic absorption spectrometry, AAS), energy dispersive X-ray analysis (EDX) and checked by ^{27}Al NMR spectroscopy. Good agreement is obtained with the three techniques (Table 1).

Table 1. Chemical and NMR characterization of various MOR samples

Sample	Si/Al			^{29}Si NMR			^{27}Al NMR		
	AAS	EDX	^{27}Al NMR	Relative intensities /% δ/ppm			Relative intensities /% δ/ppm		
				-95	-105	-110	Total [a]	T [b]	O [c]
Na-MOR	5.5	5.6	5.4	13.2	44.7	42.1	100	100	0
H-MOR-1	6.1	6.6	6.3	13.9	45.1	41.0	88	71.5	16.5
H-MOR-2	5.8	7.1	7.1	14.4	42.2	43.4	80	60.0	20.0
H-MOR-3	20.5	19.2	21.6	0	29.8	70.2	28.3	25.2	3.1
H-MOR-4	20.6	22.3	27.6	0	26.8	73.2	22.3	20.7	1.6
H-MOR-5	31.2	28.0	30.7	0	22.4	77.6	20.2	18.8	1.4

a- normalized to 100 for Na-MOR ; b- in tetrahedral and c- in octahedral coordination.

^{29}Si NMR spectra were obtained on a Bruker CXP-200 spectrometer operating in the Fourier transform mode. An r.f.-field of 49.3 Oe was used for the $\pi/2$ pulses of ^{29}Si (39.7 MHz). The conical rotor made in Delrin was spun at a rate of 3.1 kHz. Time intervals between pulse sequences were 3.0 s and 2000 free induction decays were accumulated per sample. Chemical shifts (δ in ppm) were measured from tetramethylsilane. ^{27}Al NMR spectra (without magic-angle-spinning) were recorded at 52.1 MHz. Chemical shifts in ppm were measured with respect to $Al(H_2O)_6^{3+}$ as an external reference. Time intervals between pulse sequences were 0.1 s and 5000 free induction decays were accumulated per sample.

The ^{29}Si HRMAS NMR spectrum of the parent Na-MOR sample shows a shoulder and two lines at about δ = -95, -105 and -110 ppm respectively (Figure 1). Changes in the normalized line intensities for the dealuminated samples are reported in Table 1. As the degree of dealumination increases, the shoulder at δ = -95 ppm disappears while the line intensity at δ = -105 decreases and at -110 ppm increases respectively. The ^{27}Al NMR spectrum reveals that, during dealumination, tetrahedral aluminium is removed from the zeolitic framework and part of it is deposited in the pores as hydrolyzed (i.e. octahedrally coordinated) species. The latter

are removed upon further acid treatment. Single crystal X-ray refinement[15] and DLS calculations[16] on mordenite have suggested that aluminium atoms must be located in the 4-membered rings of the mordenite structure. Using that proposal and assuming that a 4-membered ring with a single aluminium atom is more stable than the one with a double substitution, the theoretical distribution of the Al atoms in the mordenite structure can be calculated (Table 2).

Table 2. Theoretical repartition of Al atoms in the 4-membered rings in mordenite[a].

Si/Al	Al/u.c.	Number of 4-membered rings with[b]		
		2 Al	1 Al	0 Al
5.0	8	4	0	0
5.9	7	3	1	0
7.0	6	2	2	0
8.6	5	1	3	0
11.0	4	1	2	1
15.0	3	0	3	1
23.0	2	0	2	2
47.0	1	0	1	3

a- Assuming that a 4-membered ring with 2 Al is less stable than one with 1 Al, and therefore less probable.
b- A unit cell contains four 4-membered rings.

When the relative intensities of the three different arrangements so obtained are compared to those actually observed in the ^{29}Si HRMAS NMR spectra of the various dealuminated mordenites, the following assignment can be proposed : the lines at δ = -110, -105 and -95 ppm represent tetrahedral arrangements of Si (0 Al), Si (1 Al) and Si (2 Al) in the mordenite structure. Figure 2 compares the ^{29}Si NMR lines intensities corresponding to the three configurations, as a function of the Si/Al ratio in the dealuminated MOR samples. These intensities were recorded experimentally and calculated, as indicated in Table 2. Their parallel variation with the degree of dealumination confirms the assignment. The difference between the theoretical number of Si (1 Al) and its experimental value is due to the presence of silanol groups (≡ Si-OH) which also give rise to an NMR line near δ = -103 ppm in ZSM-5 zeolite[17]. Their presence was further confirmed by an IR band located near 3730 cm^{-1}, which is characteristic of defect silanol groups[18].

The variation in intensity of the ^{29}Si NMR lines during progressive dealumination of mordenite can be explained if silicon-aluminium ordering in the zeolitic framework exists. The aluminium atoms preferentially occupy the 4-membered rings. Upon dealumination with nitric acid, they are progressively eliminated from the framework and detected as octahedrally coordinated hydrolyzed species.

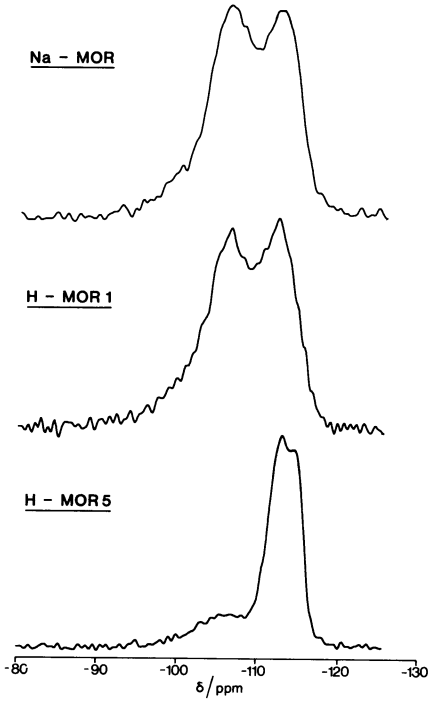

Figure 1. MAS ^{29}Si NMR spectra of mordenites : effect of dealumination.

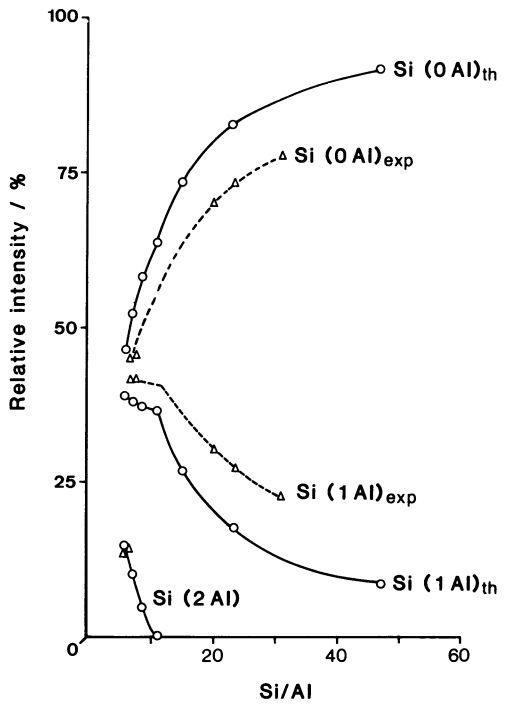

Figure 2. Variation of experimental (Δ) and theoretical (o) ^{29}Si NMR line intensities with Si/Al ratio in dealuminated mordenites.

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