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MAGIC-ANGLE-SPINNING ^{29}Si-NMR STUDY OF THE STRUCTURE OF ZSM-5 AND ZSM-11 ZEOLITES

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Eight magnetically different ^{29}Si-NMR lines are clearly distinguished in the solid state high resolution spectra of HZSM-5 zeolite with a high Si/Al ratio (1000) and some of them are assigned. The resonance line at -105 ppm in both HZSM-5 and HZSM-11 zeolites is attributed to Si atoms in the second coordination sphere of an Al atom, i.e. Si (1 Al). The -115 ppm lines stem from Si atoms in 4-membered rings. The splitting of these lines originates from a probable strain in these small rings. The incorporation of Al atom occurs exclusively in the 5-membered rings.

High resolution magic-angle-spinning (HRMAS) solid state ^{29}Si-NMR has become an outstanding tool in the structural study of zeolites. Silicon-aluminium ordering[1-5] and ring size effects[6] have been successfully analysed in the faujasite and pentasil type structures. The presence of silanol (≡ Si-OH) groups was definitely assessed in the faujasites[7] and ZSM-5 zeolites[8] by the use of cross-polarization NMR pulse sequences. Very recently, HRMAS solid state ^{29}Si-NMR has shown the structural complexity of the silicalite and ZSM-5 zeolites.[9] Nine different NMR lines suggested the presence of 24 different types of Si atoms in the repeat-unit of the structure. The present paper deals with the assignment of several ^{29}Si-NMR lines and the identification of possible aluminium sites in the ZSM-5 and ZSM-11 zeolites.

The pentasil-zeolites were synthesized according to published methods[10] using different Si/Al ratios. ^{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). Before Fourier transformations (4K data points), 2000 or 19000 free induction decays were accumulated (repetition time 3.0 s). Magic-angle-spinning (Delrin rotor) was at 3.1 kHz.

The ^{29}Si-NMR parameters (chemical shifts δ in ppm from TMS and relative line intensities in %) are listed in Table 1.

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Table 1. ^{29}*Si-NMR chemical shifts δ (ppm) and relative intensities (%) of the resonance lines in HZSM-5 and HZSM-11 zeolites.*

δ [a] (ppm) / Si/Al	Relative Intensities (%)						
	HZSM-5				HZSM-11		
	-105	-110 [b]	-113 [b]	-115	-105	-113	-115
25	-	-	-	-	16 [c]	61	23
30	13 [c]	-	74 -	13	11 [c]	67	22
50	8 [c]	-	80 -	12	8 [c]	68	24
100	4 [c]	8	75	13	5 [c]	70	25
175	0	8	79	13	0	75	25
250	-	8	79	13	-	75	25
500	-	8	79	13	-	75	25
750	-	8	79	13	-	75	25
1000	-	8	79	13	- [d]	75	25

a- Chemical shifts referred to Me_4Si as external reference.
b- The total intensities of these two lines are reported in Figure 2.
c- The Si/Al ratios are computed from $I_{total}/0.25\ I_{(-105)}$ as every Al is surrounded by 4 Si. They match exactly the experimental values.
d- Broad band centered at -103 ppm, characteristic of silanol groups.[7,8]

Figure 1 shows the spectra observed for two HZSM-5 and two HZSM-11 zeolites having very different Si/Al ratios : 30 and 1000. All spectra show essentially three resonances at -105, -113 and -115 ppm. Figure 2 illustrates the variation of the relative intensities of these lines. The -105 ppm line can be clearly identified as corresponding to an Si atom joined to one tetrahedral Al atom by an oxygen bridge i.e. Si (1 Al).[9] Its intensity decreases with increasing Si/Al ratio and drops to zero for an Si/Al ratio higher than 100. Theoretical Si/Al ratios can easily be computed from the relative intensities of this line, assuming every Al atom surrounded by four Si atoms (Table 1). The agreement is excellent for most of the samples except the HZSM-11 (Si/Al=30)where the calculated Si/Al ratio is equal to 36 . For the HZSM-11 samples an important contribution of silanol groups at -103 ppm (Figure 1,Si/Al=1000) is also observed.

The decreasing intensity of the -105 ppm line is directly linked to the increase of the -113 ppm line, while the intensity of the -115 ppm line remains constant in both HZSM-5 and HZSM-11 zeolites. In addition, the intensity ratio $I_{(-115)ZSM-11}/I_{(-115)ZSM-5}$ is equal to 2 (Table 1). This ratio is readily explained if the -115 ppm line is attributed to Si (0 Al) atoms located in 4-membered rings. Indeed, a ZSM-5 unit cell contains four 4-membered rings[11],while the ZSM-11 zeolite has eight 4-membered rings[12]. This attribution has two main consequences.

Firstly, the aluminium atoms are not located in 4-membered rings and therefore must be positioned in 5-membered rings.

Secondly, the Si(OAl) atoms in the 4-membered rings are in a state of high strain.

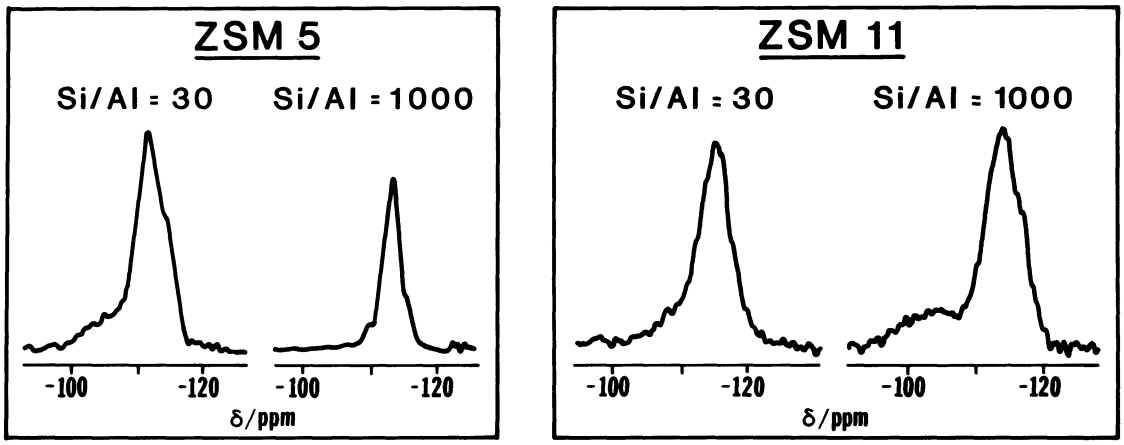

Figure 1. High resolution solid state ^{29}Si-NMR spectra of HZSM-5 and HZSM-11 zeolites with highly different Si/Al ratios.

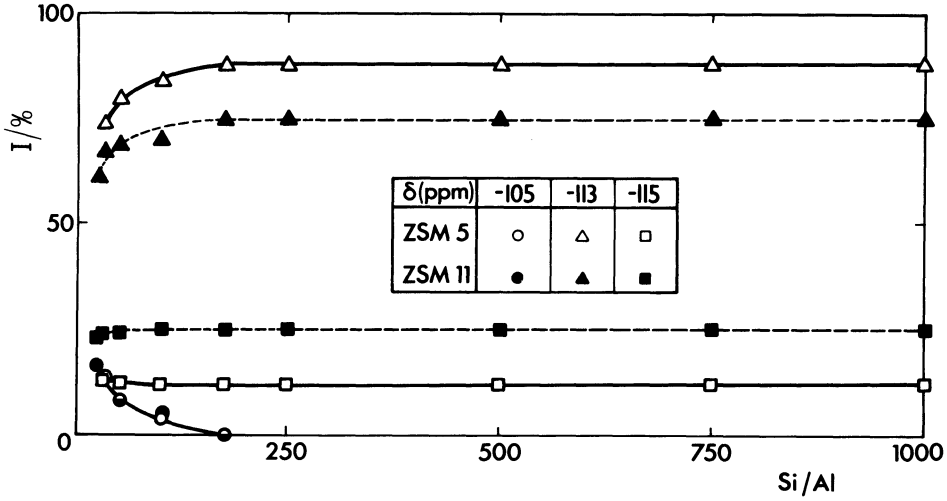

Figure 2. Variation of ^{29}Si-NMR line intensities as a function of Si/Al atomic ratios in HZSM-5 and HZSM-11 zeolites.

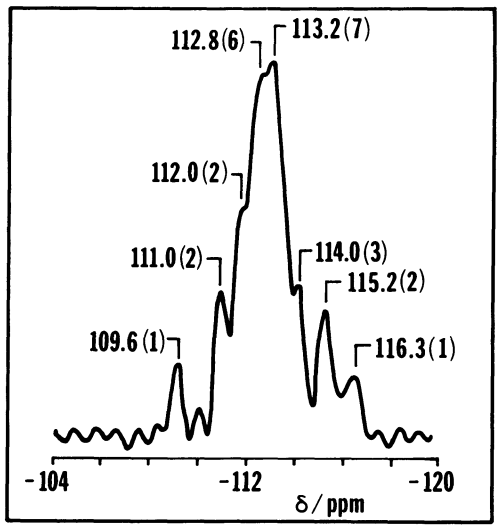

Figure 3. Resolution enhanced (LB= - 20) ^{29}Si-NMR spectrum of HZSM-5 zeolite of high Si/Al ratio (1000) (The number of Si atoms in the 24 non-equivalent sites in the repeat-unit is shown in parentheses).

Figure 3 shows the high resolution spectrum of the HZSM-5 zeolite (Si/Al = 1000). Three line-components can be distinguished in the -115 ppm region at -116.3, -115.2 and -114.0 ppm. On the basis of 24 non-equivalent sites in the repeat-unit of the ZSM-5 structure[9], the first two lines correspond to three Si atoms located in the 4-membered rings. These two lines contri-

bute to the low resolution spectra of Figure 1.

The third line at -114 ppm corresponds to the fourth Si atom in the 4-membered rings and coincides with those of two other Si atoms in 5-membered rings (vide infra). The occurrence of three magnetically different Si atoms in the 4-membered rings reveals the existence of strain in these rings. As the intensity ratio of the -115.0 ppm lines remains constant in HZSM-5 and HZSM-11 zeolites, a similar splitting can be supposed to occur in HZSM-11 but the low resolution of the spectra does not allow to distinguish between the three magnetically different sites. Although the crystal symmetries of ZSM-5 and of ZSM-11 are quite different[11,12], the magnetically different environments of the Si atoms cannot stem from different types of symmetries, but are the result of strain in the 4-membered rings.

The Si atoms in the 5-membered rings are spread over 4 ppm and give rise to six magnetically different sites : -109.6(1), -111.0(2), -112.0(2), -112.8(6), -113.2(7) and -114.0(2). The number of Si atoms in the 24 sites repeat-unit is added in parentheses. It is not possible at present to attribute these NMR lines. Nevertheless, the most intense lines at -112.8 and -113.2 ppm can be tentatively attributed to Si atoms surrounded by a set of 5-5-5-5-5-6 and of 5-5-5-5-5-10 membered rings respectively since these types of atoms are present in about 50% of the cases.[11]

As a conclusion, the present work enabled the unambiguous assignment of the -105 ppm line to Si (1 Al) atoms, and the attribution of the -114.0, -115.2 and -116.3 ppm lines to the Si (0 Al) atoms in a strained 4-membered ring. Finally, the substitution of the Si atoms by Al atoms only takes place in a 5-membered ring of the zeolitic structure, where the energy is probably lower than in the strained 4-membered rings.

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