^{29}Si Magic angle Spinning N.M.R. Investigation of Local Ordering Effects in Zeolite ZSM-39

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^{29}Si Magic angle spinning n.m.r. analysis of zeolite ZSM-39 has resolved the number of tetrahedral sites and the deviation from ideal symmetry.

The structural analogy between clathrate and zeolite frameworks is well known. $HPF_6 \cdot 6H_2O$ and $Me_4N(OH) \cdot 5H_2O$ are isostructural with sodalite[1] and the 12 Å gas hydrate is isostructural with melanophlogite.[2] ZSM-39, a high silica zeolite,[3] was found to be isostructural with the 17 Å gas hydrate.[4] The framework of ZSM-39 consists of layers of face sharing pentagonal dodecahedra (5^{12}) stacked in ABC sequence or alternately as hexakaidecahedra ($5^{12}6^4$) linked through common 6-membered rings. The arrangement of the hexakaidecahedra is the same as the sodalite cages in faujasite. The layers of ZSM-39 may also be stacked in AB sequence. The framework of ZSM-39 [5] is composed entirely of 5- and 6-membered rings and is pseudoface-centred and pseudocubic with ideal symmetry, *Fd3m* and $a = 19.36 \pm 0.02$

Table 1. ^{29}Si Magic angle spinning n.m.r. data for zeolite ZSM-39 (Si/Al = 310).

δ (p.p.m.)[a]	T-Sites per unit cell	Line width $w_{1/2}$(p.p.m.)	Relative intensity	Theoretical intensities
−108.8	$8T_1$	1.15	0.070	0.060
−113.9	$32T_2$	1.28	0.227	0.235
−117.3	$32T_3'$	1.00	0.249	0.235
−118.4	$32T_3''$	1.05	0.223	0.235
−120.3	$32T_3'''$	1.20	0.231	0.235

[a] Some samples show an extra resonance at −112.8 p.p.m. which is due to an impurity.

Å. There are weak reflections in the X-ray diffraction powder pattern which are inconsistent with *FD3m* symmetry, indicating a lower symmetry.

^{29}Si Magic angle spinning (m.a.s.) n.m.r. spectroscopy has been used to investigate local silicon environments[6] and to resolve independent sites in zeolite crystals.[7] It has recently been shown[7a,b] that the residual line broadening in the ^{29}Si m.a.s. n.m.r. spectra of these systems is a shift dispersion due to the distribution of aluminium atoms in second and further nearest neighbour sites and that sharp lines due to crystallographically inequivalent silicons in the lattice should thus be observed for highly siliceous zeolites. This paper describes a ^{29}Si m.a.s. n.m.r. analysis of ZSM-39 to resolve the symmetry and the number of T sites (*i.e.* the number of crystallographically inequivalent tetrahedral sites) in the pseudocubic framework.

Three crystallographically different sites exist in the ideal *Fd3m* structure of ZSM-39, $8(T_1)$, $32(T_2)$, and $96(T_3)$. N.m.r. spectra of ZSM-39 with Si/Al = 53.3, and 54.3 were reported to have three resonance lines at δ −109, −115, and −120 p.p.m.[8] Similar spectra have been observed for a silica analogue[9] reported to be aluminium free which also has three resonance lines (δ −112.6, −116.8, and −120 p.p.m.).[9] A similar spectrum (δ −108.9, −115.0, and −119.4 p.p.m.) has also been reported for holdstite,[10] which has the same X-ray diffraction pattern as that of ZSM-39.

Samples of ZSM-39 with Si/Al = *ca.* 285, 2400, and 310, designated (a), (b), and (c), were prepared as previously described.[3] The X-ray diffraction patterns of these samples showed weak reflections[5] which are inconsistent with *Fd3m* symmetry. The ^{29}Si m.a.s. n.m.r. spectra were obtained at 79.5 MHz on a Bruker WH-400 narrow-bore high resolution spectrometer using previously described equipment[11] and are shown in Figure 1(a)—(c). The ^{29}Si m.a.s. n.m.r. spectrum of sample (a), Figure 1(a), with three resonances (T_1, T_2, and T_3) is consistent with a structure which contains three T sites in the ratio of 4 : 32 : 96 but close examination of the T_3 resonance indicates that it consists of unresolved lines and/or a broad line. Sample (b), Figure 1(b), shows the resolution of the T_3 resonance into three components designated T_3', T_3'', and T_3'''. The ^{29}Si m.a.s. n.m.r. spectrum of sample (c), Figure 1(c), clearly shows the presence of three well defined resonances (instead of one T_3 resonance required by the ideal *Fd3m* structure) with the chemical shifts given in Table 1. There is a small associated shift of the T_2 resonance from δ −114.7, sample (a), to −113.9, sample (c). The populations of the different sites given in Table 1 were obtained from the simulation of the spectrum in Figure 1(c) as shown in Figure 1(d). The analysis of this data indicates that the T_3 site is split into three; T_3', T_3'', T_3''', by distortion due to rotation about the [111] axis with the loss of the threefold symmetry axis. There is good agreement between the measured intensities and the theoretical ones within experimental error. The lines are assumed to be due to Si(OAl) as the low Al concentration would contribute very little intensity due to Si(nAl). The agreement with theoretically predicted values supports this assumption.

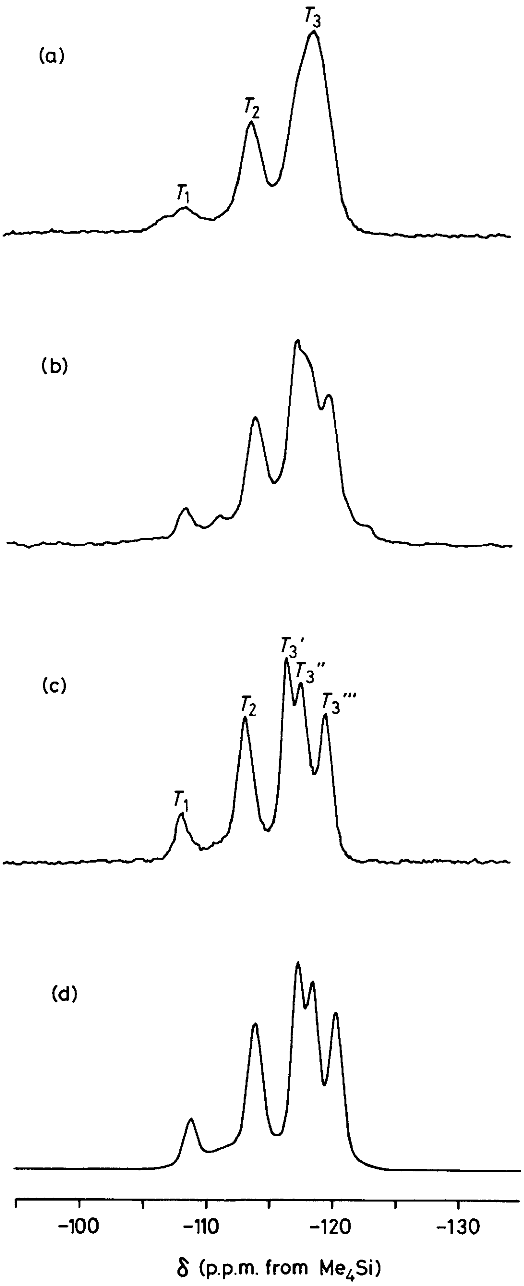

Figure 1. ^{29}Si Magic angle spinning n.m.r. spectra obtained at 79.5 MHz of zeolite ZSM-39, with differing Si : Al ratios, after calcination at 450 °C: (a) Si/Al = 285, (b) Si/Al = 2400, and (c) Si/Al = 310. (d) Computer simulation of the experimental spectrum in (c) in terms of Gaussian curves. The relative peak areas are given in Table 1. A broad Gaussian curve ($w_{1/2}$ 8 p.p.m.) centred at δ −110.0 p.p.m. was included to simulate the effect of some amorphous material in the sample.

The variation in concentration of tetrahedral Al in the three samples indicates that the Si : Al ratio does not appear to be the contributing factor in these distortions. Scanning electron microscopy shows a deviation of the crystals from the octahedral habit previously reported.[5] The presence of rods and twinning in samples (b) and (c) also indicates a change in symmetry evident in the n.m.r. spectra.

The n.m.r. spectrum of sample (a) indicates (from the width of the T_3 resonances) that the structure is disordered with distortions present which are random in nature. These distortions result in a distribution of local environments for all the T_3 sites confirming that the structure is pseudocubic. The resolution of the n.m.r. spectrum of sample (c) is greatly increased indicating a highly ordered structure but with lower symmetry in which the distribution of local environments for the T_3 sites has been resolved and there are now three unique T_3 sites of equal population. Sample (b) is intermediate in nature.

It is clearly evident that ^{29}Si m.a.s. n.m.r. can be used to resolve the effect of distortion and the deviation from ideal symmetry in zeolites.

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