^{29}Si N.M.R. Study of High Silica Tetramethylammonium-sodalite

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A correlation between the average Si–O–T† bond angle and the associated isotropic ^{29}Si chemical shift in n.m.r. spectra has been established for zeolite materials.

The dependence of the isotropic ^{29}Si n.m.r. chemical shift upon the number of Al atoms in the first co-ordination sphere of Si has been well established for many zeolites.[1–3] More recent work has shown that, in addition, factors that perturb the geometry of the Si environment have a considerable influence upon chemical shift. For example, the chemical shift of the Si(4Al) peak in the zeolite ZK-4[4,5] is coincidental with that of the Si(3Al) peak in faujasite,[2] an effect which arises from different framework topology. The influence of framework topology is also demonstrated elegantly in the case of the zeolite ZSM 5 where nine clearly resolved peaks covering a range of 6 p.p.m. are observed in the ^{29}Si n.m.r. spectrum.[6] These peaks correspond to crystallographically inequivalent Si atoms which have the same chemical environment. Large changes in chemical shift are observed when Ga is substituted for Al in the framework,[7] or when Li is substituted for Na in the interstitial sites.[8] Such changes presumably occur as a result of distortions of the Si site geometry brought about by the substitutions. Nagy and co-workers suggested that the magnitude of chemical shift may act as a probe of the type of ring species present in the structure after studying a number of zeolites containing 4-, 5-, and 6-membered rings.[9] The structures containing 5-membered rings had more shielded absorptions than those containing only 4- and 6-membered rings. In this paper I present the results of a ^{29}Si n.m.r. study of a high silica NMe$_4$-sodalite which show that information about the geometry of the Si environment may be obtained from chemical shift data, but that identification of structural units is not possible.

A high silica form of sodalite containing trapped tetramethylammonium cations was prepared from an aluminosilicate gel containing Na^+ and $(NMe_4)^+$ ions. The composition of the gel in terms of moles of oxides was 1.4 $(NMe_4)_2O$: 5.6 Na_2O : Al_2O_3 : 20 SiO_2 : 280 H_2O. The source of alumina was sodium aluminate (1.45 $Na_2O.Al_2O_3.3H_2O$, Baker) and the source of silica was a silica sol (Ludox HS40, Dupont). After heating in a sealed Teflon bottle for one week at 100 °C, the solid product was filtered, washed with H_2O, and dried in air at 100 °C. The powder *X*-ray pattern is very similar to that of NMe$_4$-sodalite[10] although the unit-cell constant, obtained by a least-squares iterative procedure, is slightly smaller. The composition of the product was determined by elemental analysis and thermogravimetric analysis to be 1.05 $(NMe_4)_2O$: 0.38 Na_2O : Al_2O_3 : 9.63 SiO_2 : 0.9 H_2O. The material contains an excess of cations $[(NMe_4 + Na)/Al > 1.0]$. This is characteristic of materials which have the sodalite structure where occlusion of anions may occur during crystallization.

The ^{29}Si n.m.r. spectrum was recorded at 39.5 MHz using the combined techniques of magic-angle spinning and proton dipolar decoupling. The spectrum is shown in Figure 1. Three resolved components are evident.‡ Assuming Loewenstein's rule,[11] and using the peak assignments shown in Figure 1, the Si : Al ratio was determined to be 4.7. The close agreement of this value with that determined from chemical analysis shows that those assignments are correct.

The chemical shifts of the three Si environments are more shielded than any so far published for structures based on the sodalite cage, namely Ga-sodalite,[7] ZK-4,[3,4] and faujasite.[2] Indeed they are coincident with the data for pentasils[6,9] suggested by Nagy *et al.* to characterize the presence of Si in 5-membered rings.

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† T = tetrahedral atom.

‡ ^{29}Si N.m.r. data for NMe$_4$-sodalite: δ (p.p.m. *vs.* Me$_4$Si) −104.6 [Si(2Al)], −110.5 [Si(1Al)], and −116.2 [Si(0Al)]; relative intensity 0.12 : 0.62 : 0.26.

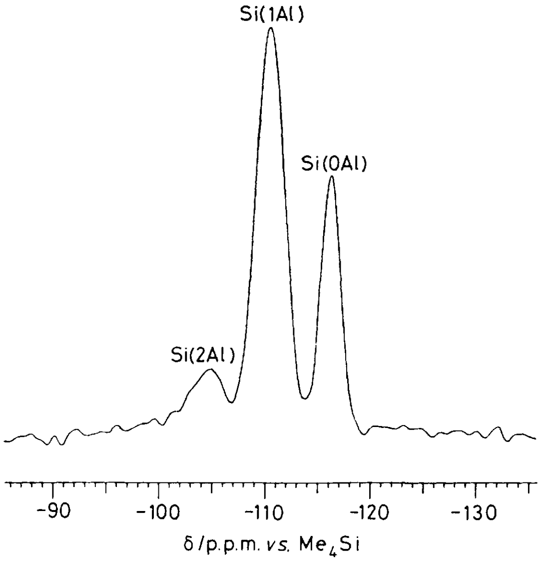

Figure 1. ^{29}Si N.m.r. spectrum with magic-angle spinning of NMe$_4$-sodalite.

Table 1. Correlation of average T–O–T angles in the sodalite cages of faujasite, ZK-4, and NMe$_4$-sodalite with chemical shift.

	Angle/°	Ref.	Chemical shift of Si(0Al) peak *vs.* Me$_4$Si/p.p.m.	Ref.
Faujasite	139	12	−103.1	2
ZK-4	148	13	−111.0	3
NMe$_4$-sodalite	158	10	−116.2	This work

Clearly, the range of chemical shift of a Si environment in a sodalite cage is wide, and there appears to be a correlation between its magnitude and the average Si–O–T angle of the environment. This is demonstrated for the Si(0Al) peak in Table 1. This remains true even when the composition dependence of the chemical shift in faujasite[14] and ZK-4[15] is considered. At higher Si–Al ratios comparable with NMe$_4$-sodalite the chemical shifts in Table 1 are deshielded by 2—3 p.p.m. This work gives substance to the observation in previous work that the Si–O–T angle may influence the chemical shift.[5] On the basis of this evidence the nature of the ring species present in the structure cannot be determined from chemical shift data alone, since the average Si–O–T angles for Si in 4-, 5-, and 6-membered rings cover the same broad range.[16]

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