

Evidence for Secondary Building Unit Effects on the Solid State ^{29}Si N.M.R. Resonance of Silicon in Zeolitic Structures

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Summary Zeolites which contain five-membered rings of silica tetrahedra (HZ mordenite, Na-ZSM-5, and H-ZSM-11) present a ^{29}Si -n.m.r. line at *ca.* -113 p.p.m. in contrast with other zeolites which do not contain this building unit (Na-A, Na-X, Na-Y, and H-L), for which resonance occurs in the -80 to -106 p.p.m. range, depending on the Si:Al ratio.

THE great sensitivity of the ^{29}Si -n.m.r. chemical shifts to molecular environment and to the type of condensation of silica tetrahedra, as well as their gradual variation with the degree of silicon substitution by aluminium,¹ suggested recently that the structure of zeolite A might have to be reconsidered.^{2,3} In particular, it was proposed that the mode of preparation could influence the ordering of aluminium in the framework⁴ and that Loewenstein's rule⁵

would not strictly apply in this case, the presence of Al-O-Al bridges being inferred from the n.m.r. data.

Pentasil materials (ZSM-5- and ZSM-11-type zeolites) are characterized by a highly siliceous content and by the occurrence of five-membered rings of silica tetrahedra in their secondary building unit.⁶ The latter component is also present in mordenite, while other zeolites such as Linde type A, X, Y, and L contain four- and six-membered rings as secondary building units.⁷ We have examined these structures by high resolution solid state ^{29}Si n.m.r. and have identified a resonance which, we believe, characterizes silicon in five-membered ring units. It demonstrates the usefulness of the technique for the characterization of materials with low Al content and offers new means to probe the type of secondary building units present in zeolitic frameworks.

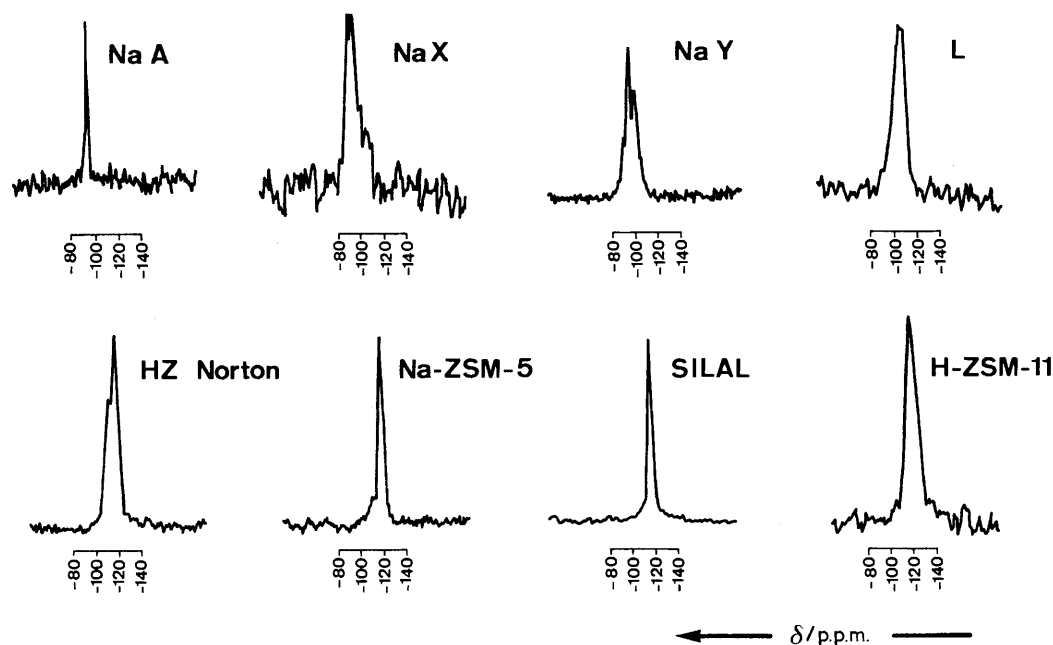


FIGURE. High resolution solid state ^{29}Si -n.m.r. spectra obtained from various zeolites, as indicated. Chemical shifts are referred to Me_4Si .

^{29}Si -N.m.r. spectra were obtained at 29.7 MHz with magic angle spinning. A 20° spin-rotation was achieved using 3.5 Oersted radio frequency pulses, with 0.15 s intervals. 10^4 free induction decays were accumulated before Fourier transformation. Typical linewidths were 1–2 p.p.m., higher values indicating the presence of inhomogeneities in the sample or a lower crystallinity. The spectra obtained are shown in the Figure and chemical shift values are listed in the Table. Relative intensities (in parentheses) and Si:Al ratios and orderings are also mentioned.

TABLE. ^{29}Si -N.m.r. chemical shifts of zeolites.

Zeolite type	Si:Al ratio	^{29}Si Chemical shift ^a (Rel. int.)	Si(<i>n</i> Al)-ordering <i>n</i> -value
Na-A	1.14 ^b	-89.2(100)	3
Na-X	1.25 ^c	-84.8(33), -89.4(33)	4,3
		-96.0(15), -98.6(11)	2,1
		-106.6(8)	0
Na-Y	2.4 ^c	-88.9(18), -94.1(42)	3,2
		-98.8(30), -105.3(10)	1,0
H-L	3.0 ^c	-98.6 ^d	1
H-Z Norton	9.0 ^e	-106.6(38), -112.2(51)	0,0
		-102.0(11)	1
(Na, H)-ZSM-5 ^f	12.3 ^e	-106.4(12), -112.7(88)	? ,0
		-115.7(sh.) ^g	0
		-113.9(100)	0
SILAL	49.9 ^e	-113.9(100)	0
H-ZSM-11	36.8 ^e	-112.4 ^h	0

^a Chemical shift values referred to Me_4Si . ^b Personal communication from Dr. P. A. Jacobs. ^c Approximate values from D. W. Breck, 'Zeolite Molecular Sieves,' Wiley, New York, 1974. ^d Broad peak, linewidth = 13 p.p.m. ^e Experimental values determined by proton-induced γ -ray emission. ^f Partially protonated sample following calcination of the organic compound containing precursor at 773 K. ^g sh = shoulder; intensity not estimated. ^h Broad peak, linewidth = 11 p.p.m.

In the A-, X-, Y- and L-type frameworks, the T (and therefore Si)-atoms occupy corners of four-membered rings. These materials have ^{29}Si -n.m.r. resonances in the -80 to

-106 p.p.m. range, the chemical shift values of which are determined by the Si(*n* Al) ordering of the silica tetrahedra (*n* = 0, 1, 2, 3, or 4). Lippmaa *et al.*¹ demonstrated the ^{29}Si shift dependence on the number of aluminium-centred tetrahedra linked to silicon *via* oxygen bridges, while they are almost unaffected by the nature of the cation present. We observe a Si(3 Al) ordering for our zeolite Na-A which, however, has a Si:Al ratio well above unity and therefore may well not disobey Loewenstein's rule. A range of Si(*n* Al) orderings (see the Table) is observed for Na-X and Na-Y, in agreement with recent reports in the literature.^{2,3,8} Zeolite H-L has a resonance centred at -98.6 p.p.m., corresponding to an Si(1 Al) ordering. It is, however, rather broad and probably arises also from the presence, in lesser amounts, of the Si(2 Al) and Si(0 Al) configurations.

In H-Z Norton mordenite, a shoulder and two distinct ^{29}Si lines are observed at -102.0, -106.6, and -112.2 p.p.m., respectively, with corresponding intensities of 11, 38, and 51. It is well known that mordenite has two types of T-sites in the ratio 1:2 and it is tempting to relate somehow the latter distribution to the former observation. It is, however, well appreciated that its framework contains both four-membered and five-membered rings and following the previous discussion, it seems logical to assign the -106.6 p.p.m. peak to Si atoms with Si(0 Al) ordering in four-membered rings. The shoulder at -102.0 p.p.m. could be ascribed to the corresponding Si(1 Al) configuration. The Si resonance at -112.2 p.p.m. should hence characterize Si in five-membered rings, probably in the Si(0 Al) ordering as well. This assignment, however, implies that the Si(1 Al) five-membered ring configuration could also contribute to the -106.6 p.p.m. resonance as a result of the paramagnetic shift occurring upon substitution of Si by Al.

This assignment finds support in our observations on highly siliceous (little Al-substitution effect) pentasil-type

zeolites: ZSM-5 that is partially Na-exchanged [(Na, H)-ZSM-5], ZSM-11 in the protonated form (H-ZSM-11), and silicalite⁹ treated by AlCl₃ to incorporate some aluminium in its framework SILAL.¹⁰ The observation of resonances near -113 p.p.m. for these materials which have a majority of five-membered rings in their frameworks shows clearly that the Si(0 Al) configuration in five-membered rings leads to a ²⁹Si resonance in the -112 to -114 p.p.m. region. The broader signal observed for H-ZSM-11 may result from inhomogeneities but it could also reflect a more important contribution of Si(0 Al) configurations from four-membered rings (in agreement with its known structure).^{6,7} The lower intensity resonance observed at -106.4 p.p.m. in (Na, H)-ZSM-5 may result from Si(1 Al) configurations in five-membered rings and/or Si(0 Al) ordering in four-membered rings as discussed for mordenite, but it could also originate from silanol groups at the surface or occluded in the zeolite. There seems to be a qualitative correlation between the occurrence of the shoulder observed at about -116 p.p.m. and higher sodium (and possibly aluminium) contents.

Although these data demonstrate the ability of ²⁹Si-n.m.r. spectroscopy to probe the nature of secondary building units in zeolites, it still needs to be explained why there is a shift in the Si(0 Al) resonance when either a four- or five-membered ring is considered. Spectra obtained from cyclic siloxanes in solution indicate the occurrence of a diamagnetic shift with greater ring size,^{11,12} with however only a small

difference between five- and six-membered rings. The diamagnetic shift of ²⁹Si in the four-, to five-, to six-membered ring series stems from the increasing contribution of the sp³ orbitals. The latter is accompanied by a higher mean excitation energy from the electronic ground state and a larger extension in space of the Si 3p-orbital. Both effects decrease the paramagnetic contribution to the chemical shift, hence the observed diamagnetic shift. The possible contribution of d-orbitals has not been demonstrated unambiguously so far.¹³

In addition to the previously reported effect of the degree of silicon substitution by aluminium on the ²⁹Si chemical shifts and its application to the characterization of classical zeolites with a reasonably high Al-content (Si:Al = 1-3), we have hence shown that the technique can also be applied successfully to investigate highly siliceous zeolites such as pentasil materials and, in particular, that it can bring information on the occurrence of five-membered rings of silica tetrahedra in such crystalline frameworks. It also probes the various types of building units as shown for different zeolites.

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