Ordering of Silicon and Aluminium Ions in the Framework of NaX Zeolites. A Solid-state High-resolution ^{29}Si N.M.R. Study

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Summary ^{29}Si N.m.r. has provided detailed information on silicon–aluminium ordering of the aluminosilicate framework of zeolites which showed that the arrangement of silicon and aluminium ions of an NaX zeolite with Si/Al 1·4 is not centrosymmetrical.

ALTHOUGH the framework structure of NaX zeolites is well known from *X*-ray studies,[1] direct information concerning the ordering of silicon and aluminium ions in the aluminosilicate framework is difficult to obtain because of the close similarity in *X*-ray scattering power of Si and Al. In two recent papers[2,3] we have shown that solid-state high-resolution ^{29}Si n.m.r. spectroscopy is a useful new method for the investigation of the framework structure of aluminosilicates, including the problem of silicon–aluminium ordering. The ^{29}Si n.m.r. spectra of aluminosilicates show distinct signals for the five possible numbers of AlO_4 tetrahedra connected to the SiO_4 tetrahedra. The presence and quantitative distribution of the central silicon atoms in the five building units $Si(OSi)_{4-n}(OAl)_n$, designated as Si(*n*Al) ($n = 0$—4), can be estimated from chemical shifts and relative signal intensities. On the other hand, the Si(*n*Al) distribution can be derived from structural models with certain Si–Al ordering. From a comparison of both distributions the accuracy of the Si–Al ordering in the model structure can be tested.

From an idealized X-type zeolite structure with Si/Al 1 : 1 (12 Si and 12 Al ions per sodalite cage) and regularly alternating Si and Al ions throughout the framework, the Si/Al 1·18 zeolite (13 Si and 11 Al ions per sodalite cage) can be derived formally by symmetrical replacement of one Al for one Si atom in each sodalite cage. This process generates two six-rings per sodalite unit with two Al ions in the *meta*-positions and no subsequent rearrangement of the Al and Si ions is possible.[4] This structure gives an Si(*n*Al) distribution of Si(0Al) : Si(1Al) : Si(2Al) : Si(3Al) : Si(4Al), 1 : 0 : 0 : 4 : 8, respectively, which has been shown to be in adequate agreement with the intensity distribution of the corresponding signals in the ^{29}Si n.m.r. spectrum.[3] Small deviations can be explained by some irregularities in the Si–Al ordering of the real structure of the investigated zeolite sample.

For the NaX zeolite with Si/Al 1·4 (14 Si and 10 Al ions per sodalite cage) a second Al ion must be replaced by Si in each sodalite cage and different possibilities of Si–Al ordering occur. Referring to the work of Dempsey,[4] the second substitution (Si for Al) should occur as far as possible from the first one, *i.e.* at the inverse position through the centre of the sodalite cage. A detailed investigation of structural models with that arrangement of Si and Al ions indicated an Si(*n*Al) distribution of 1 : 0 : 0 : 4 : 2 ($n = 0$—4, respectively) which is obviously different from the intensity distribution found in the ^{29}Si n.m.r. spectrum, shown in Figure 1.

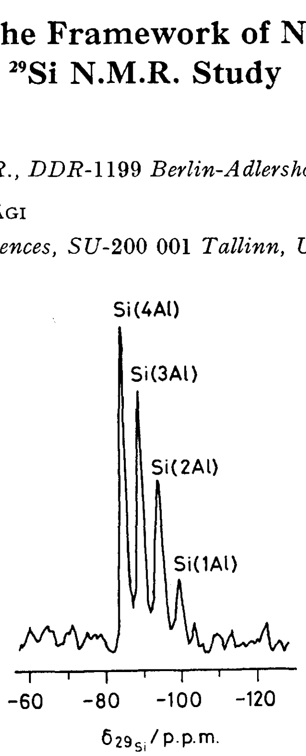

FIGURE 1. ^{29}Si N.m.r. (tetramethylsilane) spectrum of NaX zeolite with Si/Al 1·4.

However, a close agreement between the Si(*n*Al) distribution of the structural model and the intensity distribution of the spectrum can be obtained if the Si and Al ions are rearranged as shown in Figure 2. This structure contains two six-rings with two Al atoms in the *para*-positions, one of which is part of the hexagonal prism which connects two sodalite units (site I six-ring) and the other one is part of the supercage structure (site II six-ring). A careful examination of this structure gives an Si(*n*Al) distribution of 0 : 2 : 3 : 4 : 5 ($n = 0$—4, respectively) which agrees well with the signal-intensity ratios found in the ^{29}Si n.m.r. spectrum (Figure 1). It is interesting to note that Dempsey *et al.*[5] conclude, from a detailed discussion of distinct breaks in the plot of crystal lattice parameters *versus* Si/Al ratios of sodium X and Y zeolites, that similar *meta* → *para* rearrangements occur only at an Si/Al ratio $\geqslant$ 1·67 (15 Si and 9 Al ions per sodalite cage). However, from the plot shown in ref. 5 it is obvious that the break occurs at Si/Al 1·4, which confirms the result of our ^{29}Si n.m.r. study.

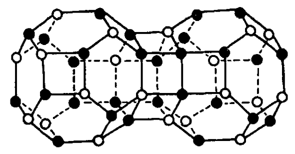

FIGURE 2. Schematic representation of silicon–aluminium ordering of NaX zeolite with Si/Al 1·4. Si, ●; Al, ○. Oxygen atoms not shown.

The foregoing results show that the ^{29}Si n.m.r. spectra can give detailed information on the Si–Al ordering; this can be used to supplement X-ray structure studies of zeolites. Further studies of a series of faujasite-type zeolites with Si/Al ratios up to 5, and of dealuminated and stabilized Y zeolites will be reported elsewhere.

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