

^{29}Si Magic Angle Spinning N.M.R. Spectroscopy as a Probe of the Uniqueness of Zeolite Framework Structures

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The high field (9.4 T) ^{29}Si magic angle spinning n.m.r. spectra of highly siliceous ZSM-5 and ZSM-11 clearly demonstrates the uniqueness of these two zeolites, which have very similar lattice structures.

Zeolites, which are framework aluminosilicates usually with characteristic channels and cavities,¹ have wide application as sorbents and catalysts and are of considerable commercial importance, especially in the petroleum industry.² X-Ray diffraction is the primary tool for the determination of the structures of these materials³ but is limited in several important ways. Firstly, since Si and Al have almost identical X-ray scattering factors the location of individual silicon and aluminium atoms cannot be uniquely determined although the overall lattice structure may be described. Secondly, many synthetic zeolites are microcrystalline in nature precluding the application of conventional single crystal X-ray diffraction techniques. Although recent synchrotron based X-ray diffraction experiments⁴ indicate that it may be possible in the future to work with much smaller crystals, to date most literature data especially for synthetic zeolites have come from powder X-ray diffraction measurements. The data available from these experiments are limited and quite different structures may give very similar diffraction patterns because of the coincidence of major repeat distances within the structures, often making it difficult to decide whether two zeolite preparations have yielded identical species or not. We have used ^{29}Si magic angle spinning (m.a.s.) n.m.r. spectroscopy of highly siliceous zeolites as a probe of their framework structures and illustrate the results with the ZSM-5/ZSM-11 system. We propose that it be used in conjunction with diffraction techniques to decide whether a given zeolite has a unique structure.

Zeolites ZSM-5 and ZSM-11 are both based on the pentasil unit shown in Figure 1(a). Pentasil units are joined to form

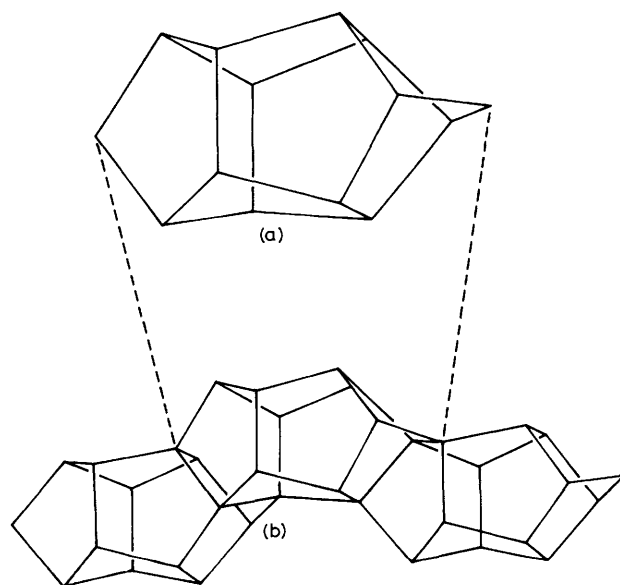


Figure 1. Schematic representation of (a) the pentasil unit, (b) a chain formed by interlocking pentasil units.

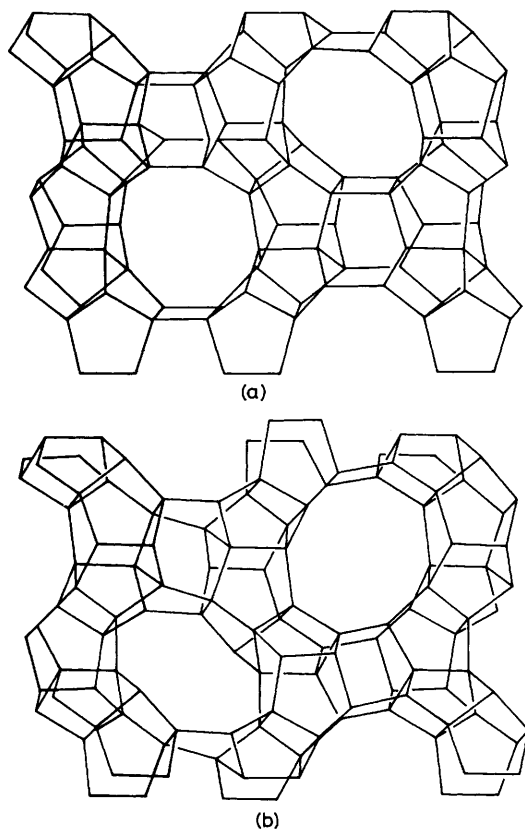


Figure 2. The structures of (a) zeolite ZSM-11 and (b) zeolite ZSM-5. The pentasil chains are outlined.

columns [Figure 1(b)] and these columns are linked such that adjacent columns are related by reflection and form the basic layer unit in the two structures, Figure 2. When these layers are linked such that neighbouring pairs are related by reflection the ZSM-11⁵ framework is formed, Figure 2(a), while linking the layers so that they are related by an inversion centre results in the ZSM-5⁶ framework, Figure 2(b). As can be seen from Figure 2, the structures of the two zeolites are quite different, as are their physical and physicochemical properties. However, enough of the major repeat distances are the same so that their powder X-ray diffraction (x.r.d.) spectra are similar [Figure 3, (c) and (d)].

A clear distinction may be made by ²⁹Si m.a.s. n.m.r. spectroscopy. This technique has provided structural information complementary to that from diffraction data⁷ and has recently been reviewed.⁸ Early work centred on the study of zeolites of low Si/Al ratio but it has recently been found that considerable information may be obtained from the study of highly siliceous systems.⁹⁻¹² In these systems, formed either by direct synthesis or by dealumination reactions, very narrow resonances are observed in the ²⁹Si m.a.s. n.m.r. spectra. From the excellent resolution of these spectra, which can be obtained for a variety of systems, the mechanism of the residual line broadening may be deduced.⁹ This high resolution also allows interpretation of the spectra from systems with more than one crystallographic site,¹⁰ as well as revealing the effects of lattice distortions,¹¹ and sorbed organic molecules.¹²

Most importantly in the present application of these experiments, the narrowness of the resonances in the spectra make it possible to observe separate signals from crystallographically inequivalent silicon atoms in the unit cell and the chemical shift values and relative intensities of these signals provide a unique 'fingerprint' of the structure of the zeolite.

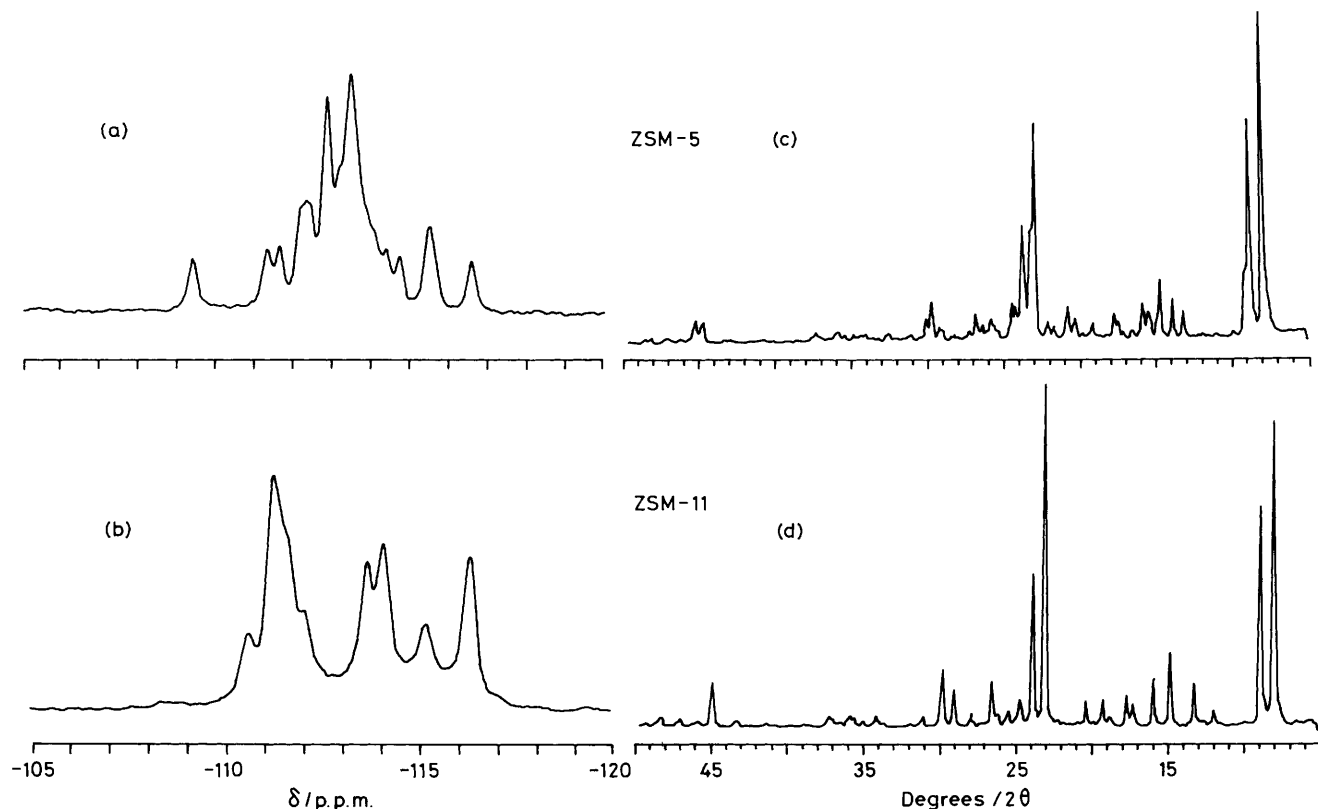


Figure 3. (a) and (b) The ²⁹Si m.a.s. n.m.r. spectra obtained at 79.5 MHz of samples of highly siliceous ZSM-5 and ZSM-11 respectively, prepared by hydrothermal dealumination techniques. Spectra are referenced to Me₄Si at δ 0 p.p.m. (c) and (d) The corresponding powder x.r.d. patterns of the same samples.

Since the ^{29}Si n.m.r. spectrum is determined by local geometries, it reflects the unit cell structure in a different and complementary manner to the powder x.r.d. data. This is illustrated in Figure 3 (a) and (b), which show the ^{29}Si m.a.s. n.m.r. spectra of highly siliceous samples of ZSM-5 and ZSM-11 in the acid form prepared by hydrothermal dealumination.¹³ Although the powder X-ray diffraction patterns of the two species are similar, reflecting the high proportion of identical repeat distances in the two structures, the ^{29}Si m.a.s. n.m.r. spectra are different and diagnostic of the structures, reflecting the different space groups and local site geometries therein. The ZSM-11 sample is unique: it is difficult to prepare ZSM-11 free of ZSM-5 intergrowths of mixtures, but both the x.r.d. and ^{29}Si n.m.r. data indicate that very little, if any, ZSM-5 material is present in the highly siliceous ZSM-11 sample. Transmission electron microscopy of this material should substantiate this conclusion.

In the case of highly siliceous ZSM-5, the ratio of the intensities of the outermost resolved peaks to the total intensity is 1:24, indicating that there are 24 crystallographically unique silicon atoms in the unit cell, compatible with the space group $P2_12_12_1$.^{14a} In the case of ZSM-11, the ratio of the highest field peak to the total intensity is 1:6.4, in reasonable agreement with the proposed structure⁵ which has seven crystallographically unique silicon atoms of relative intensities 8:16:16:16:16:8:16 which yields a ratio of 1:6. As in the case of ZSM-5,¹² sorbed organic molecules induce changes in the ^{29}Si m.a.s. n.m.r. spectrum of highly siliceous ZSM-11 which are characteristic of the sorbate. A detailed interpretation of the ^{29}Si m.a.s. n.m.r. spectra of both ZSM-5 and ZSM-11 and the effect of sorbed organic molecules on each system will be presented elsewhere.¹⁵

In this case, the ^{29}Si m.a.s. n.m.r. spectra clearly reflect the uniqueness of the ZSM-5 and ZSM-11 lattices. Alternatively, the spectra could show that systems thought to be different have, in fact, identical lattice structures. For example, it has been shown that ZSM-5 and Silicalite have the same basic lattice structure.¹⁴

^{29}Si m.a.s. n.m.r. spectra of highly siliceous zeolite systems are diagnostic of their lattice structures in terms of local environments and should be used in conjunction with X-ray diffraction studies to provide a description of the structures of unknown systems.

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