

The Effect of Temperature on the ^{29}Si Magic Angle Spinning N.M.R. Spectrum of Highly Siliceous ZSM-5

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^{29}Si magic angle spinning n.m.r. experiments on highly siliceous ZSM-5 have shown that there is a phase transition in the temperature range 295–363 K in agreement with the results of powder X-ray diffraction measurements.

Recently, ^{29}Si and ^{27}Al magic angle spinning (m.a.s.) n.m.r. investigations of zeolites have added substantially to our understanding of the structures of these species.^{1,2} Particularly useful has been the study of the ^{29}Si m.a.s. n.m.r. spectra of highly siliceous systems prepared either by direct synthesis or by dealumination reactions.³ The removal of aluminium gives rise to very narrow lines (~ 1 p.p.m.) in the ^{29}Si n.m.r. spectrum;⁴ the resulting high-resolution spectra are very sensitive probes of the structures of the unit cells reflecting the effects of crystallographic inequivalence,⁵ the uniqueness of closely related unit cells,⁶ and the effect of stacking faults.⁷

In the course of our investigations of details of the structure of zeolite ZSM-5^{8,9} we have found that the ^{29}Si m.a.s. n.m.r. spectra of highly siliceous samples give highly resolved and very characteristic spectra.^{10,11} The sorption of low loadings of organic molecules within a certain size range causes substantial changes in the spectrum indicative of a change of the monoclinic structure to an orthorhombic one characteristic of the sorbed molecule, a result confirmed by powder X-ray diffraction (x.r.d.) measurements.¹² Subsequent work indicates that the change occurs over a small concentration range,¹³ supporting a phase transition as the mechanism.

Previously, we have found temperature variation in high-resolution solid-state n.m.r. experiments to be an important variable in the investigation of solid-state structures¹⁴ and have implemented a series of experiments to determine the effect of temperature on the ^{29}Si , ^{27}Al , and ^{23}Na m.a.s. n.m.r.

spectra of zeolites. In this communication we present our preliminary findings on the effect of temperature on the ^{29}Si m.a.s. n.m.r. spectra of highly siliceous ZSM-5. A recent publication by Hay and Jaeger¹⁵ reports the effect of temperature on the powder x.r.d. patterns of a variety of ZSM-5 samples and these data are complementary to the results presented here.

Figures 1(a)–(d) show the effect of temperature on the ^{29}Si m.a.s. n.m.r. spectra of a sample of very highly siliceous as-synthesized ZSM-5 calcined to remove the organic matrix. Figure 1(a) shows the spectrum obtained at ambient temperature and is characteristic of the monoclinic form of the structure as previously described,¹⁰ the peak intensities indicating the presence of 24 silicon atoms in the unit cell. As the temperature is raised, complex changes occur with the limiting high-temperature spectrum being obtained at 363 K. Spectra obtained at 383 and 393 K were identical to the 363 K spectrum shown in Figure 1. The spectral changes are reversible; on cooling to room temperature the original spectrum is obtained. The limiting high-temperature spectrum shown in Figure 1(d) can be deconvoluted in terms of 6 overlapping peaks as shown in Figure 2(a,b). The ratio of the highest field peak to the total spectral intensity is 1:11.9, in good agreement with the ratio of 1:12 expected from the postulated structure for the orthorhombic form.⁹ Further, the spectrum is similar to that of an uncalcined sample of highly siliceous ZSM-5 prepared by the 'fluoride-silicalite' method¹⁶

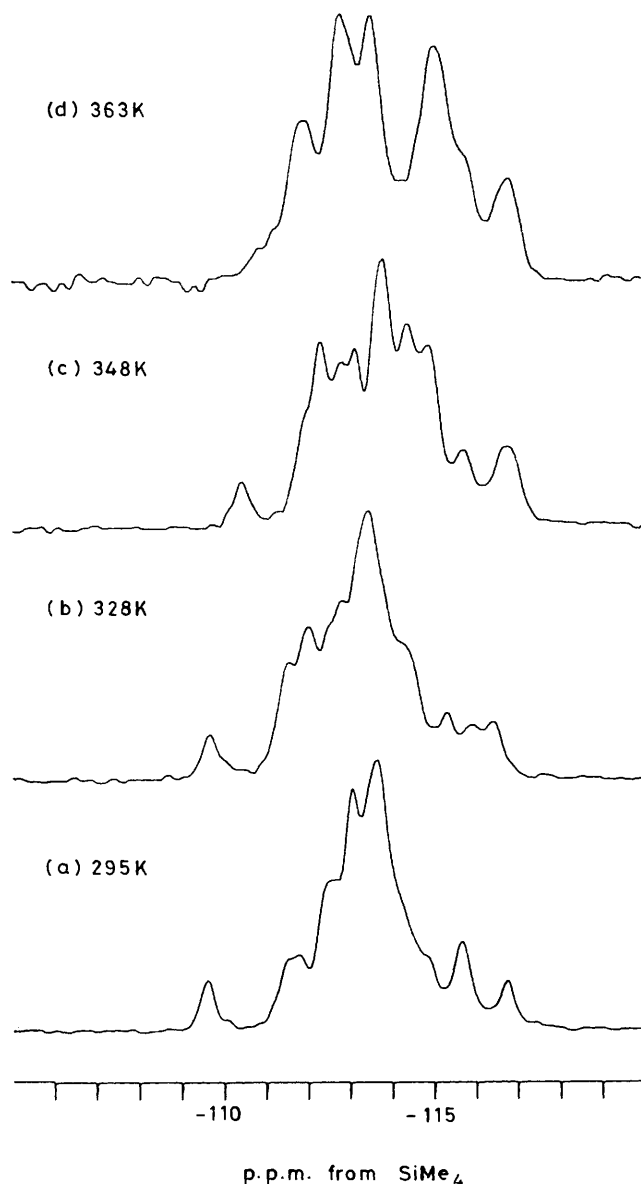


Figure 1. ^{29}Si M.a.s. n.m.r. spectra (79.5 MHz) of a highly siliceous ZSM-5 sample at the temperatures indicated.

shown in Figure 2(d). This sample is known to be orthorhombic¹⁷ and the similarity between the two spectra is additional evidence that the limiting high-temperature spectrum is that of the orthorhombic structure, the peak positions reflecting the numbers and geometries of the crystallographically inequivalent silicons in the unit cell, the better resolution being due to the lower aluminium content of the sample.

The spectra thus indicate a phase transition from a monoclinic to an orthorhombic form of the ZSM-5 sample, in agreement with the power x.r.d. data of Hay and Jaeger.¹⁵ The temperature range over which the changes are observed (~295 to 363 K) is somewhat larger and higher than that reported by these authors for a highly siliceous sample, but the temperature of the change is strongly dependent on the aluminium content and it is probable that the present sample has a somewhat lower concentration of aluminium. The spectra obtained at intermediate temperatures indicate that the change is a gradual one as the temperature gradient over

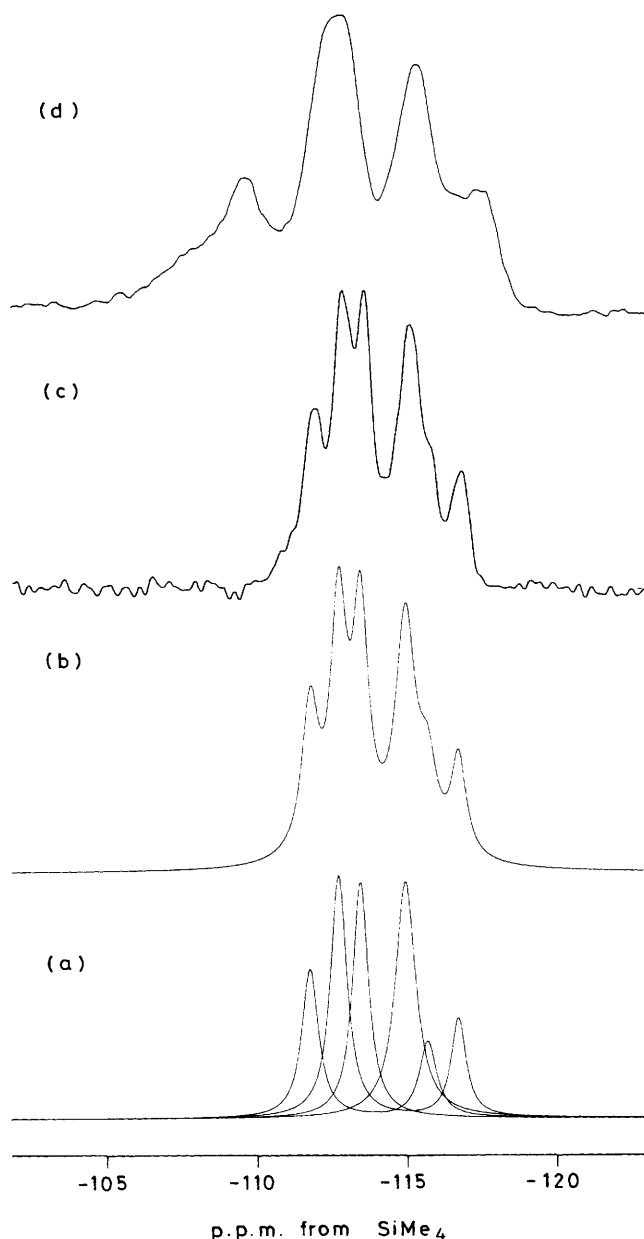


Figure 2. (a) Deconvolution of the high-temperature limiting ^{29}Si m.a.s. n.m.r. spectrum in terms of overlapping Lorentzian peaks. (b) Simulated spectrum from addition of peaks in (a). (c) Experimental limiting high-temperature spectrum (363 K, 79.5 MHz). (d) ^{29}Si M.a.s. n.m.r. spectrum (79.5 MHz) of an uncalcined 'fluoride silicalite' sample (ambient temperature).

the sample is ~5 K. Different highly siliceous ZSM-5 samples yield the same limiting high- and low-temperature ^{29}Si m.a.s. n.m.r. spectra, but the intermediate spectra may differ and it is not possible at present to give a detailed description of the mechanism of the transition.

We are continuing these investigations including the effect of sorbed organic molecules which are thought to lower the transition temperature and the effect of much larger temperature variations on the m.a.s. n.m.r. spectra of zeolitic materials.

Added in proof. More recent spectra exhibiting even higher resolution than those presented here indicate that the coales-

cence of the two peaks to form the highest field resonance in Figure 1(d) is not quite exact and the exact unit cell probably contains 24 independent T-atoms in the absence of sorbed organic molecules.

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