

## Characterization of a High-loaded Intercalate of *p*-Xylene with a Highly Siliceous Form of ZSM-5 by High Resolution $^{29}\text{Si}$ Solid-state NMR Spectroscopy

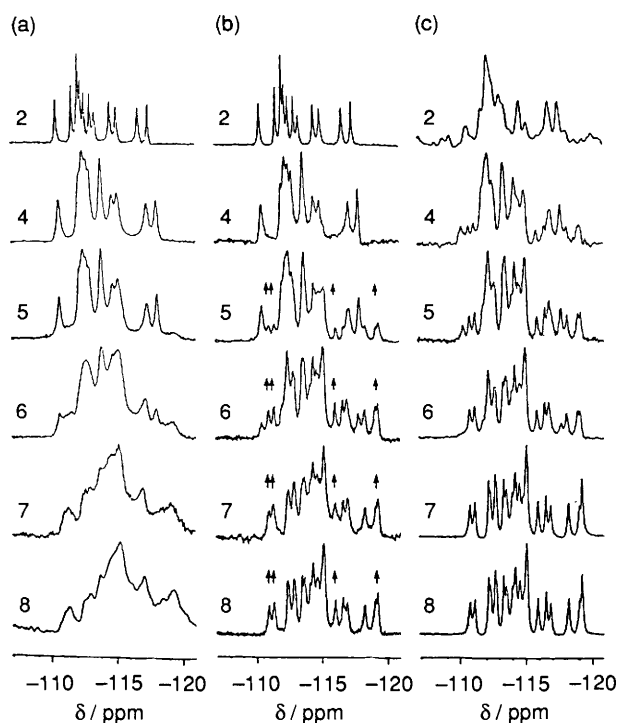
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High-resolution solid-state  $^{29}\text{Si}$  MAS NMR spectra of zeolite ZSM-5 with 4–8 molecules of sorbed *p*-xylene per unit cell reveal the presence of a 'high-loaded' phase for this system in which there are 24 T sites in the asymmetric unit; proton decoupling must be used to obtain good resolution in this phase and this is an indication for considerable dipolar interaction between the *p*-xylene protons and the  $^{29}\text{Si}$  nuclei in the zeolite lattice, in contrast to the case of the 'low-loaded' form with two molecules per unit cell previously observed and described; thus, cross-polarization may be used to discriminate in favour of the 'high-loaded' phase.

In the development of high-resolution  $^{29}\text{Si}$  solid state MAS NMR spectroscopy as a complementary technique to diffraction studies for the investigation of zeolite structures,<sup>1</sup> considerable attention has been paid to zeolite ZSM-5<sup>2</sup> and the effects of temperature and sorbed organic molecules<sup>1,3–8</sup> on its structure. These latter systems are of interest because of the demonstrated selectivity of the adsorption process in terms of the size and shape of the organic sorbates.<sup>9</sup> For example, *p*-xylene is easily and efficiently incorporated into the zeolite lattice, while the *o*- and *m*-isomers are not. Increasing the temperature has been shown to induce a change from the monoclinic form with 24 T-sites to an orthorhombic form with

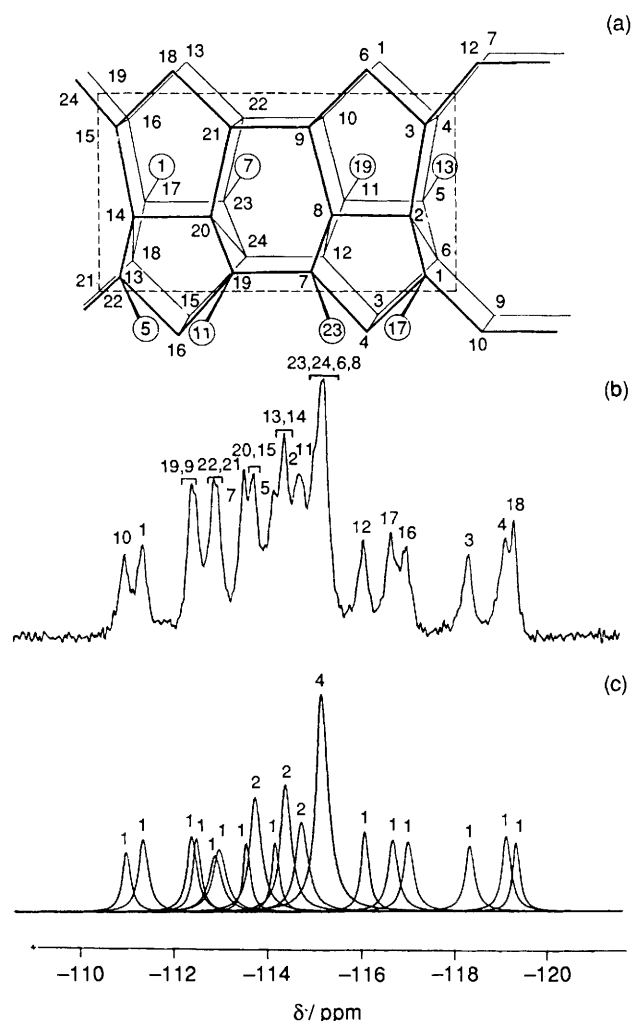
12 T-sites.<sup>9</sup> A similar phase-change is produced by the sorption of *p*-xylene, the change being complete at approximately two molecules per 96 T-atom unit cell (uc) and with high enough spectral resolution, the complete three-dimensional phase diagram of the combined effects of temperature and *p*-xylene concentration can be determined from NMR studies.<sup>7</sup> Previous sorption studies indicate, however, that up to eight molecules of *p*-xylene per uc may be incorporated into the zeolite ZSM-5 lattice<sup>10,11</sup> and a recent complete single crystal *X*-ray diffraction study by van Koningsveld and co-workers<sup>12</sup> indicates a structure of orthorhombic symmetry at high *p*-xylene loadings but with 24 T-sites. Previous NMR



**Figure 1(a).**  $^{29}\text{Si}$  MAS NMR spectra of ZSM-5 with increasing concentration of *p*-xylene. The numbers indicate the numbers of *p*-xylene molecules sorbed per 96 T atom uc. (b)  $^{29}\text{Si}$  MAS NMR spectra with proton decoupling during acquisition of the same samples. 350 s Delay between pulses ensures the spectra are quantitative. (c)  $^{29}\text{Si}$  CP/MAS NMR spectra of the same samples.

studies were characterized by line-broadening effects with no clear indication of the presence of a new phase.<sup>13–14</sup> We have further explored the effect of higher loadings of *p*-xylene in ZSM-5 and in the present communication we report the  $^{29}\text{Si}$  NMR characterization of an additional 'high-loaded' phase for this system.

Figure 1(a) shows the effect of adding increasing amounts of *p*-xylene on the  $^{29}\text{Si}$  MAS spectra of a completely siliceous sample of ZSM-5 obtained without proton decoupling as in previous studies. From 2 to 8 molecules per unit cell were incorporated by direct addition and equilibrated at 100 °C in sealed tubes. The spectrum at 2 molecules per uc is identical to that previously described and indicates clearly that the asymmetric unit contains 12 T-atoms. As more *p*-xylene is added, there is a gradual broadening of the spectra, most noticeably in the bases of the resonances, consistent with previous investigations but no clear indication of the formation of another species. Figure 1(b) shows the  $^{29}\text{Si}$  MAS spectra of the same series of samples but with proton decoupling used during acquisition. There is now substantial narrowing of the spectra and a second species is clearly observed at loadings greater than 4 molecules per uc as indicated by the vertical arrows. Its relative proportion gradually increases with increasing *p*-xylene concentration and it is the only species present at loadings greater than ~7 molecules per uc. The delay times used were such that the spectra may be considered to be quantitatively reliable. The spectrum of this new 'high-loaded' form clearly indicates that there has been a further change of symmetry. In addition, both phases clearly co-exist and the sharpness of all of the resonances indicates that both are highly ordered. The need for proton decoupling in order to obtain narrow resonances



**Figure 2(a).** Schematic representation of the asymmetric unit of 'high-loaded' form of *p*-xylene/ZSM-5 as indicated by the dashed lines. (b)  $^{29}\text{Si}$  MAS NMR spectrum with proton decoupling of the high-loaded form of *p*-xylene/ZSM-5 with the assignment of the individual resonances. (c) The individual Lorentzian curves from a deconvolution of Figure 2(b). The numbers above the curves indicate the relative peak intensities.

suggests that cross-polarization<sup>15</sup> from the  $^1\text{H}$  nuclei in the *p*-xylene sorbates to the  $^{29}\text{Si}$  nuclei in the framework might be reasonably efficient for this 'high-loaded' structure in contrast to the situation for the 'low-loaded' orthorhombic phase where cross-polarization is very inefficient. Figure 1(c) shows the  $^{29}\text{Si}$  CP MAS NMR spectra corresponding to the spectra in Figures 1(a), (b). There is considerable enhancement both of the S : N and also of the relative intensities of the signals from the 'high-loaded' phase. These spectra show no evidence for exchange between the two forms and the discrimination in the cross-polarization process reflects a difference in the dynamic properties of the *p*-xylene sorbate molecules in the two phases. Figure 2(b) shows a  $^{29}\text{Si}$  MAS spectrum with proton decoupling of the sample loaded with 8 molecules of *p*-xylene per uc. A long relaxation delay ( $\geq 5$  times the longest  $^{29}\text{Si}$   $T_1$  of ~70 s) between successive scans was used to ensure quantitatively reliable signal intensities. The deconvolution presented in Figure 2(c) clearly shows that the asymmetric unit contains 24 T-sites. This is in agreement with the recent single-crystal X-ray study by van Koningsveld and co-workers<sup>12</sup> who

concluded that the ZSM-5 structure at very high loadings of *p*-xylene was orthorhombic, space group  $P2_12_12_1$ , with 24 inequivalent T-sites. The postulated structure is shown in Figure 2(a). The complete assignment of T-sites and  $^{29}\text{Si}$  NMR resonances indicated in Figure 2(b), has been made on the basis of  $^{29}\text{Si}$  2D NMR investigations which will subsequently be reported in detail in a full paper.<sup>16</sup> Further work in this area should now make it possible to fully describe the structures of the sorbate-lattice complexes and perhaps elucidate the details of the interactions between them.

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