Sorbate-induced Structural Changes in ZSM-5 (Silicalite)

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The high-field (9.4 T) ^{29}Si m.a.s. n.m.r. spectrum (m.a.s. = magic angle spinning) of highly siliceous ZSM-5 (silicalite) shows that changes in the zeolite structure occur when sorbate molecules are present; these changes occur at low loading levels and are characteristic of the nature of the sorbed molecules, and *X*-ray diffraction confirms that the effect is a perturbation of the zeolite structure itself.

There has recently been considerable interest in the use of ^{29}Si and ^{27}Al m.a.s. n.m.r. for the elucidation of the structures of zeolites (m.a.s. = magic angle spinning).[1] In the present work we demonstrate that the presence of sorbed molecules can cause changes in the zeolite framework structure. In the course of investigations into the mechanisms of dealumination reactions by these techniques,[2] it was observed that there was a dramatic change in the ^{29}Si high-field (9.4 T) m.a.s. n.m.r. spectrum of a highly siliceous ZSM-5 (silicalite), which shows a number of Si[OAl] resonances due to crystallographically inequivalent silicon atoms in the unit cell (Figure 1a), when acetylacetone (Hacac) was present as sorbate (Figure 1f).

As can be seen from Figure 1 (d, e, and f), which show the high-field (9.4 T) ^{29}Si m.a.s. n.m.r. spectra of silicalite samples with different sorbed molecules (sealed with Teflon tape to minimize loss of sorbate), this is quite a general effect, different sorbed molecules causing different and characteristic changes in the ^{29}Si m.a.s. n.m.r. spectrum. The sharpness of the spectra indicate that there is no loss of crystallinity. In general, as illustrated for the case of *p*-xylene in Figures 1b and 1c, the change occurs at very low loading levels of sorbate (2 µl of liquid per 250 mg of zeolite), which is less than one molecule per unit cell, and quickly reaches the limiting spectrum (10 µl of liquid per 250 mg of zeolite). This effect is not observed in the ZSM-5 as synthesized loaded with the tetra-alkylammonium template.

The spectral changes are reversible; on heating the sample *in vacuo*, the original spectrum (Figure 1a) is obtained. The same changes are observed with lower Si : Al ratio material (down to Si : Al = 35 : 1) although the spectra are broader owing to the effect of the aluminium.[3]

The effect of the sorbed molecules on the ^{29}Si spectrum is thought to be due to modification of the lattice structure, since no effect is observed when *p*-xylene is sorbed into highly siliceous mordenite, Y, or omega zeolites, whereas changes would have been observed if they were due to general susceptibility effects of the sorbed organic molecules replacing water in the cavities. This is confirmed by the changes in the corresponding powder *X*-ray diffraction (X.R.D.) patterns shown in Figure 1(g—l) (the region 2θ 22 to 25° is expanded for clarity) obtained with the samples sealed with collodion film to minimize loss of sorbate. The zeolites were prepared for both n.m.r. and X.R.D. experiments by sealing them in vials, adding the liquid sorbates with a syringe through the septum seal, and allowing them to equilibrate. After the addition of *p*-xylene, pyridine, and Hacac, Figure 1 (c, e, and f), identical ^{29}Si m.a.s. n.m.r. spectra were obtained before and after the X.R.D. patterns were recorded, indicating that no loss of sorbate occurred in transferring the material from the vial to the spinner. The changes observed in the peaks at 2θ = 23.3 and 23.8° clearly indicate, in agreement with the n.m.r. data, that structural changes causing lattice distortion are occurring *which are characteristic of the sorbate used,* while the sharpness of the peaks indicates that the sample crystallinity is maintained, and the lowering in relative

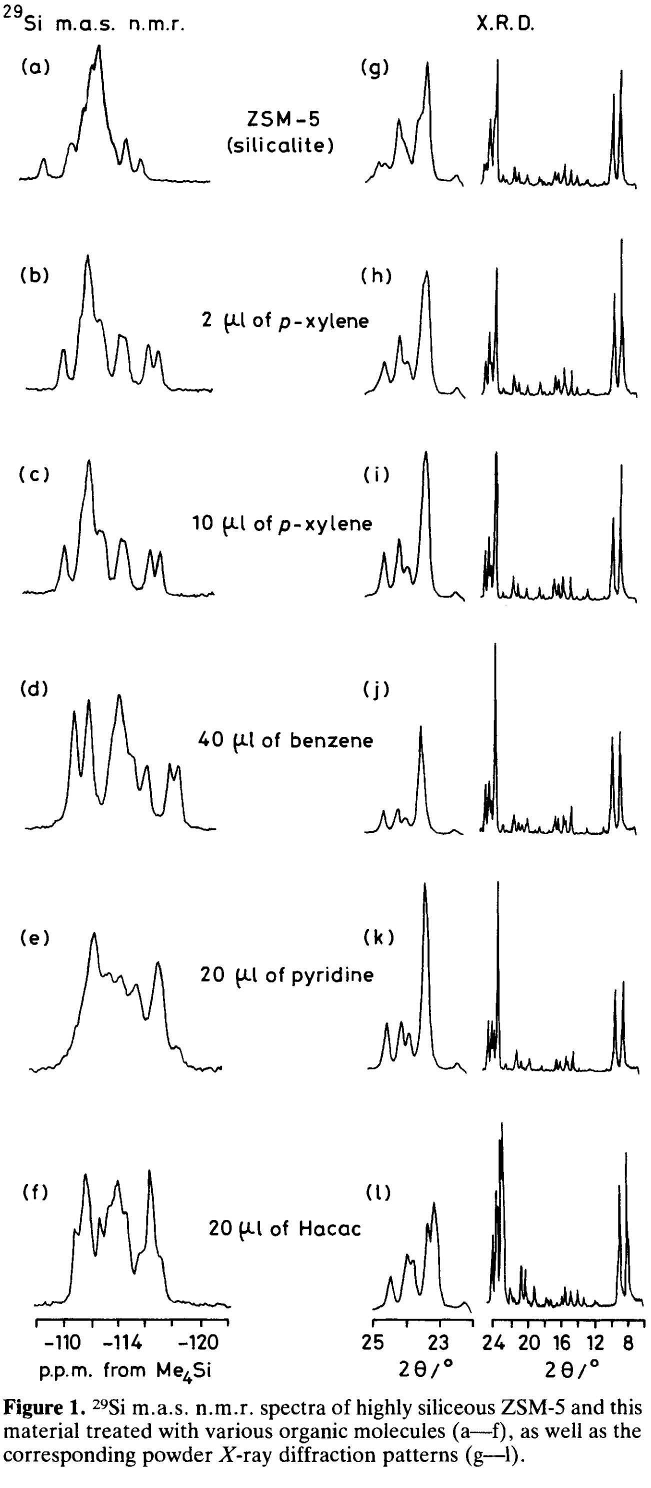

Figure 1. ^{29}Si m.a.s. n.m.r. spectra of highly siliceous ZSM-5 and this material treated with various organic molecules (a—f), as well as the corresponding powder *X*-ray diffraction patterns (g—l).

intensity of the two low angle peaks ($2\theta = 7.9$ and $8.9°$) reflects the presence of sorbate. The first change which occurs (Figure 1i) is the loss of the doublet splitting of the peak at $2\theta = 24.4°$, *indicative of a change* from a monoclinic to an orthorhombic symmetry[4] while the subsequent appearance of different and characteristic patterns in the range $2\theta = 23$—$24°$ indicates changes in the cell dimensions. Similar limiting X.R.D. patterns are observed with ZSM-5 (Si : Al = 35 : 1) although the initial X.R.D. pattern now reflects orthorhombic symmetry to begin with and no longer shows the splitting at $2\theta = 24.4°$.

Thus, there is a consistency between the n.m.r. and X.R.D. results, both of which indicate that the presence of low loadings of sorbate molecules cause structural changes characteristic of the sorbed species. The effect may not be restricted to the ZSM-5 (silicalite) system studied here but it is certainly not completely general. Further work may show if the sorbtion causes a distortion of the four- and six-membered rings, inducing translocation of the pentasil chains.

Added in proof: Changes in the ^{29}Si m.a.s. n.m.r. spectra of silicalite with different sorbed molecules from those described here have been independently observed (Dr. G. W. West, personal communication) but not interpreted in terms of structural changes.

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