Orthorhombic–Monoclinic Phase Changes in ZSM-5 Zeolite/Silicalite

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X-Ray diffraction experiments have shown that the framework symmetry change between monoclinic and orthorhombic nature, exhibited in ZSM-5 zeolite depends not only on the aluminium concentration and on the presence of sorbate molecules, but also on the temperature of the sample.

The change in symmetry from orthorhombic to monoclinic of the highly siliceous end-member of the ZSM-5 zeolite series (silicalite) on ion-exchange or calcination[1] has been related to the sodium and aluminium contents[1,2] and sorbate induced factors.[1] During the characterization of ZSM-5 zeolite, we observed that these structural changes are also temperature dependent. Thus the temperature of samples during measurements must be specified when other parameters of ZSM-5 zeolite are being related to its structure.

Samples of ZSM-5 zeolite ($50 < SiO_2:Al_2O_3 > 3000$), prepared in the presence of tetrapropylammonium bromide by the method of Argauer and Landolt,[3] were calcined at 798 K for 10 h and exchanged to the protonated form by reflux in 0.5 M HCl for 14 h. Powder *X*-ray diffraction (x.r.d.) measurements were carried out on such calcined and protonated samples at selected temperatures in the range 262—798 K in a helium atmosphere using a Siemens D500 diffractometer (entrance slits 0.3° and 0.3°, exit slits 0.3° and 0.018°, Cu-K_α radiation). This communication summarises the results obtained.

For silicalite ($SiO_2:Al_2O_3 > 3000$) the peak positions in x.r.d. traces measured over the range $7° < 2\theta < 35°$ at 298 K matched those calculated from a monoclinic model in space-group $P2_1/n$[1] whilst at 325 K the positions matched those calculated from an orthorhombic model, space group $Pn2_1a$ or *Pnma*.[1] As shown in Figure 1, the 133 and $13\bar{3}$ peaks (at 2θ = 24.5—25.0°) are separated in the monoclinic but not in the orthorhombic pattern, whilst the separation between the 051 and 501 peaks (at 2θ = 23.0—23.5°) is more obvious in the orthorhombic pattern than in the monoclinic pattern. The orthorhombic form is retained up to 798 K. Furthermore, if the sample temperature is alternated anywhere between, say, 298 K and a value in the range 335—798 K, the diffraction pattern changes reversibly between monoclinic and orthorhombic.

For ZSM-5 zeolite, increasing the aluminium concentration above a critical value decreases the temperature (T_t) at which the monoclinic–orthorhombic phase change occurs. For example, whilst for $SiO_2:Al_2O_3$ ratios > 460 (< 0.2% wt. Al) T_t is the same as for silicalite (317—325 K), for $SiO_2:Al_2O_3 = 198$ (0.44% wt. Al) $T_t = 295$ K, and for $SiO_2:Al_2O_3 < 110$ (> 0.8% wt. Al) T_t is < 272 K.

For silicalite, adsorption of linear hydrocarbons of chain length $>C_4$ into the framework decreases T_t. For example, if the chain length is between 7 and 12, T_t is in the range 283—293 K, a decrease of *ca.* 30 °C. However, adsorption of different hydrocarbons such as benzene, cyclohexane, or monosubstituted benzenes, and of small molecules, such as ethanol, methanol, or water, does not alter T_t. In all cases changes in unit cell dimensions on absorption are apparent from the x.r.d. traces, particularly in the orthorhombic case, as has been observed by others.[4]

The result that $T_t < 295$ K for $SiO_2:Al_2O_3 < 198$ is in agreement with the findings of Nakamoto and Takahashi,[2] that calcined ZSM-5 zeolite was orthorhombic for $SiO_2:Al_2O_3 < 160$ and monoclinic for $SiO_2:Al_2O_3 > 160$ (presumably measured at room temperature). However, the suggestion of Wu *et al.*[1] that water vapour may cause relocation of residual sodium species enabling the framework structure to undergo the symmetry change seems unlikely, because the present results show that the change takes place in the absence of water vapour.

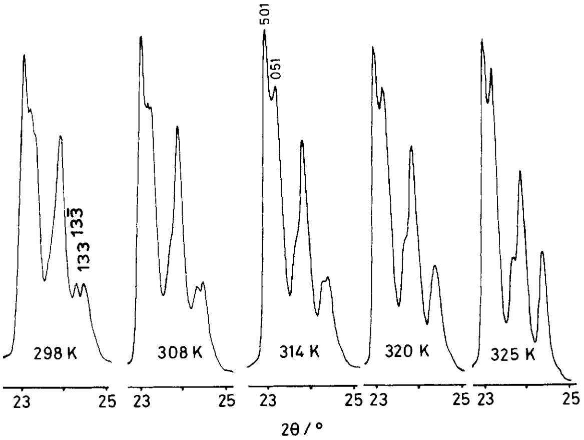

Figure 1. Powder x.r.d. traces (scan rate 0.5 deg min^{-1}) of silicalite ($SiO_2:Al_2O_3 > 3000$) showing the changes from monoclinic to orthorhombic structure. The sample was calcined and protonated, and then maintained at the indicated temperatures under helium.

High resolution ^{29}Si magic angle spinning (m.a.s.) n.m.r. spectra of calcined silicalites both with and without adsorbed species have been reported by various authors[5,6] and it has been shown that the spectrum of pure silicalite can be simulated by a minimum of nine gaussian signals.[5] Attempts have been made to relate the spectrum to the structure.[5,6] In view of the present results, it would be desirable to measure ^{29}Si m.a.s. n.m.r. spectra of ZSM-5 zeolite at selected temperatures above and below T_t in order to determine if the ^{29}Si m.a.s. n.m.r. spectrum depends on the structure in the manner suggested by Fyfe *et al.*[5]

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