Hydrothermal Conversion of Piperazine–ZSM-39 into Tetrapropylammonium-silicalite-1

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The hydrothermal conversion of the clathrasil PIP–ZSM-39 into the silica molecular sieve precursor TPA-silicalite-1 (PIP = piperazine, TPA = tetrapropylammonium) has been followed by *X*-ray powder diffraction and pH measurements.

The silica molecular sieve precursor TPA-silicalite-1 [*MFI* structure, unit cell composition $(TPAOH)_4(SiO_2)_{96}$] is prepared by the hydrothermal crystallisation of alkaline reaction mixtures that contain tetrapropylammonium (TPA) template ions.[1—4] The source of SiO_2 is invariably an amorphous solid (added directly to the reaction mixture or precipitated *in situ*) that is considerably more soluble than the crystalline product. The essential condition for the formation of TPA-silicalite-1 is that the solubility product, $[TPA^+]^4[OH^-]^4[Si(OH)_4]^{96}$, should be exceeded. Thus, provided the composition of the solution phase is suitable, *i.e.* high $[TPA^+]$ and $[OH^-]$ concentrations, crystallisation should occur even when the SiO_2 source is a crystalline solid with a solubility comparable to that of the molecular sieve. To test this proposition we have attempted the crystallisation of TPA-silicalite-1 from reaction mixtures in which the only source of SiO_2 is the dense clathrasil PIP–ZSM-39 (*MTN* structure, PIP = piperazine).[5,6]

PIP–ZSM-39 was crystallised at 180 °C in a stirred autoclave from the reaction mixture [15 PIP, 20 SiO_2, 250 H_2O (SiO_2 = Merck Kieselgel 60 35—70 ASTM silica gel)].[7] The product

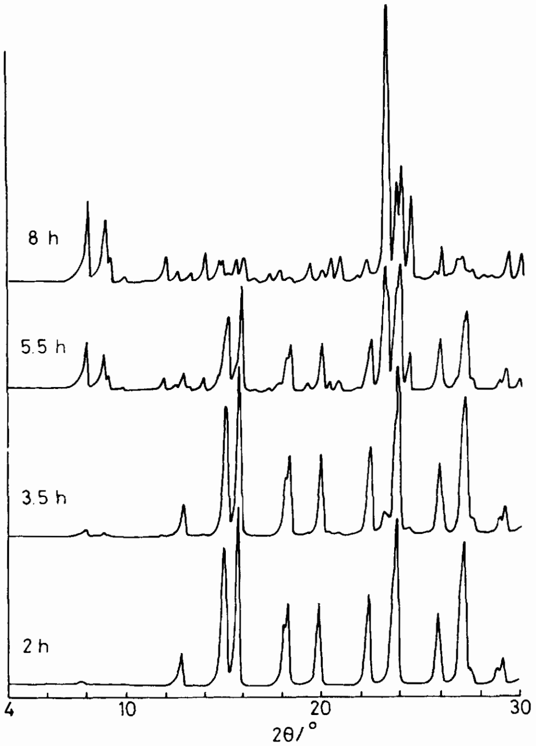

Figure 1. *X*-Ray powder diffraction patterns of samples taken during the conversion of PIP–ZSM-39 (2 h) into TPA-silicalite-1 (8 h) in a solution of NaOH + TPABr.

obtained after 21 days was pure highly crystalline PIP–ZSM-39 with 8—10 μm octahedral crystals.[5] Chemical analysis gave 89.38% SiO_2 which is consistent with a unit cell composition of $(PIP)_8(SiO_2)_{136}(H_2O)_{15.8}$ [ideal composition $(PIP)_8(SiO_2)_{136}(H_2O)_{16}$].[6] The washed, as-made PIP-ZSM-39 was dispersed in an aqueous alkaline solution of tetrapropylammonium bromide and the conversion into TPA-silicalite-1 was carried out at 150 °C in a stirred (300 r.p.m.) 500 cm^3 stainless steel autoclave. Samples were taken throughout the reaction and after pH measurement[8] the solid phase was separated, washed, equilibrated with water vapour, and examined by *X*-ray powder diffraction.

Figure 1 shows the *X*-ray diffraction patterns of samples taken during the crystallisation of TPA-silicalite-1 from the reaction mixture 5 NaOH, 2 TPABr, (17.9/136) $[(PIP)_8(SiO_2)_{136}(H_2O)_{15.8}]$, 1000 H_2O. Approximate percentage crystallinities (Figure 2) estimated[4] from the peak heights of the sharp lines at $2\theta = 15.1$ and 15.8° for PIP-ZSM-39 and 23.1° for TPA-silicalite-1 show that there is an initial induction period of approximately 2 h and that the crystallisation is complete within a further 6 h. The pH measurements (Figure 2) show an initial sharp drop corresponding to the rapid partial dissolution of the clathrasil, a constant value during the crystallisation, and a sharp rise corresponding to the removal of silica from the solution phase during the final stages of the reaction. As the pH observed during the reaction has the constant value established in the induction period it appears that the rate of conversion is controlled by the growth of the TPA-silicalite-1 rather than the dissolution of the clathrasil. The general pattern of behaviour is similar to that observed when amorphous silica is used[2,8] and is entirely consistent with the growth of TPA-silicalite-1 from the solution phase rather than by the solid phase transformation of the clathrasil. This is borne out by optical and scanning electron microscopy; the diminution of the clathrasil crystals and the growth of those of the molecular sieve could be clearly observed. Although the crystallisation took about the same time as one[9] carried out

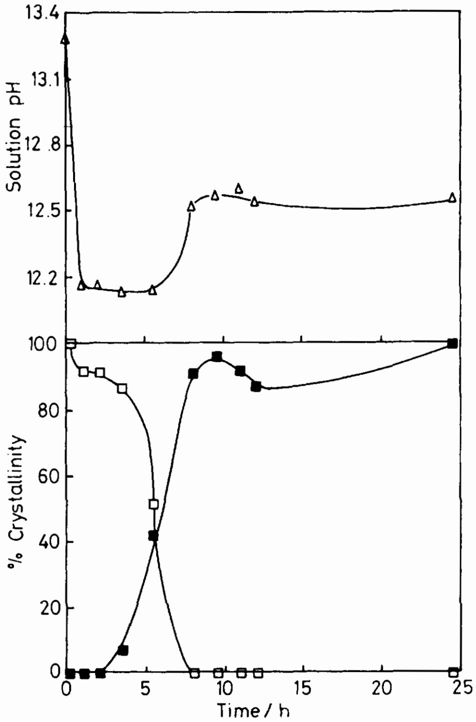

Figure 2. Crystallinity and pH (△) profiles for the conversion of PIP–ZSM-39 (□) into TPA-silicalite-1 (■) in a solution of NaOH + TPABr.

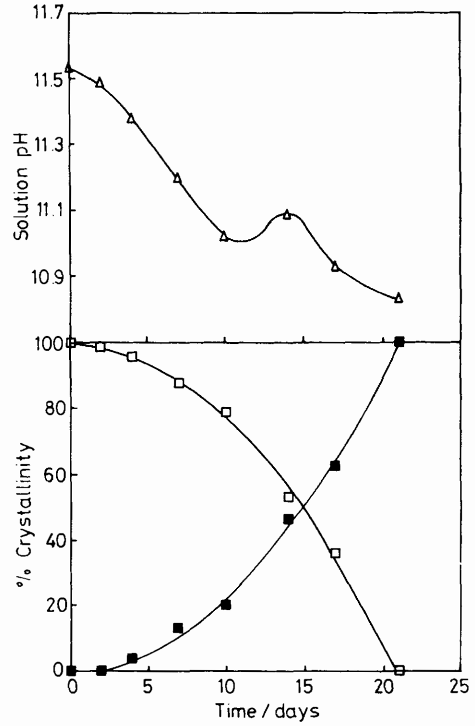

Figure 3. Crystallinity and pH (△) profiles for the conversion of PIP–ZSM-39 (□) into TPA-silicalite-1 (■) in a solution of PIP + TPABr.

under identical conditions with fumed silica (Cab-o-sil M5, BDH Ltd) it gave much larger crystals (12 × 10 × 4 μm compared with 7 × 5 × 2 μm). The smaller crystals are consistent with the higher supersaturation and the consequent increased nucleation in the amorphous silica system.

Figure 3 shows the results obtained with the reaction mixture 10 PIP, 2 TPABr, (17.9/136) $[(PIP)_8(SiO_2)_{136}(H_2O)_{15.8}]$,1000 H_2O. The replacement of NaOH by the weak base piperazine leads to a reduction in the pH of the solution phase[10] and consequently the reaction is much slower (21 days compared with 8 h). The drop in pH during the crystallisation arises from the incorporation of TPAOH into the TPA-silicalite-1 structure, according to equation (1). The reaction was much slower than one[4] carried out under identical conditions with fumed silica (21 compared with ~4 days), probably because the solubility of the clathrasil {solubility product $[PIP]^8[Si(OH)_4]^{136}$} is supressed by the piperazine in the solution phase. The TPA-silicalite-1 crystals were elongated (25 × 5 × 3 μm) and typical of those produced under adverse conditions (*e.g.* low pH).

$$(96/136)\ [(PIP)_8(SiO_2)_{136}] + 4\ TPA^+ + 4\ H_2O \rightarrow [(TPAOH)_4(SiO_2)_{96}] + (224/136)\ PIP + 4\ PIPH^+ \quad (1)$$

In high silica zeolite synthesis the formation of dense silicas, *e.g.* quartz, either directly or by recrystallisation of the product molecular sieve, is a common occurrence. In contrast, the present work shows that the conversion of a dense structure (*MTN*, 18.7 T-atoms per nm^3) into an open one (*MFI*, 17.9 T-atoms per nm^3) is readily achieved. Indeed in the solutions used for this work, even quartz is slowly converted into needle shaped crystals of TPA-silicalite-1. That such conversions are possible reflects the high degree of stability conferred on the *MFI* structure by the TPA ion. Similar conversions of dense phases to open framework ones also occur with low silica zeolites (*e.g.* Na-analcime, *ANA* structure, 18.6 T-atoms per nm^3 into species P, *KFI* structure, 14.7 T-atoms per nm^3)[11] but in this case inorganic salts are used as the void filling agents.

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