

## Crystallisation of Silicalite-1 Precursors

Stuart G. Fegan and Barrie M. Lowe\*

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, U.K.

The composition of the (Na, TPA) (TPA = tetrapropylammonium) precursor to silicalite-1 is determined by the base content of the reaction mixture, and for both low and high base contents the crystallisation is accompanied by apparently anomalous pH changes.

High silica zeolites are less soluble in water than the amorphous aluminosilicate gel solids from which they are crystallised and hence their formation is normally associated with an increase in pH.<sup>1,2</sup> A simple theoretical treatment shows that the pH rise and the yield of zeolite both decrease when the base content of the reaction mixture is increased.<sup>2</sup> The present investigation into the crystallisation of the precursor to silicalite-1<sup>3-5</sup> provides the first systematic set of experimental observations against which this theory may be tested.

Silicalite-1 precursors were crystallised at 95 °C in stirred polypropylene reactors from the mixtures  $x\text{Na}_2\text{O} \cdot 2\text{TPABr} \cdot 20\text{SiO}_2 \cdot 1000\text{H}_2\text{O}$  (TPA = tetrapropylammonium,  $0.25 < x < 6.5$ ,  $\text{SiO}_2 = \text{Cab-o-sil M5}$ ). The pH values of samples taken throughout the crystallisation were determined<sup>1</sup> and the final solid products were washed, dried, equilibrated with water vapour, and examined by X-ray powder diffraction, X-ray fluorescence, and thermal gravimetric analysis. All the reaction mixtures, except that with  $x = 0.25$ , gave pure well crystallised products with organic contents close to the ideal unit cell composition  $4\text{TPAOH} \cdot 96\text{SiO}_2$ . The mixture with  $x = 0.25$  contained insufficient base for complete crystallisation and its percentage crystallinity (63%) estimated from X-ray powder diffraction measurements was close to the maximum

(60%) that could be produced if all the crystalline material had the ideal unit cell composition.

The highest yields (Figure 1) were obtained as predicted<sup>2</sup> from the reaction mixtures that had the lowest base contents. These high yields were not however accompanied by the large increases in pH required by the theory. For  $x = 0.5$  and  $0.7$  the calculated<sup>2</sup> increases in pH are in the ranges 0.78–0.99 and 0.75–0.94 whereas the experimental values are –2.77 and –0.04 respectively. Only for the higher base contents  $x = 2$  and  $x = 3.5$  are the experimental values (0.78, 0.72) in good agreement with the calculated ones (0.69–0.84, 0.66–0.80).<sup>2</sup> The apparently anomalous decrease in pH obtained for  $x = 0.5$  and  $0.7$  and the abnormally small increases (0.42, 0.42) obtained for  $x = 0.85$  and  $1.00$  are readily interpreted as a consequence of base occlusion. The cations in the silicalite channels must be associated with hydroxide ions or broken siloxane bonds  $\{\equiv\text{Si}-\text{O}^- \text{HO}-\text{Si}\equiv\}$ ; in either case hydroxide ions are removed from the solution phase, and for reaction mixtures with low base contents their removal has a dominant effect on the pH. This is much less significant for reaction mixtures with high base contents and so in these cases there is a reasonable agreement with the theory. For the highest base content the pH increase (0.22) is again less than the calculated value (*ca.* 0.70) but in this case the discrepancy probably arises from an increase in the solubility of the crystalline solid consequent on the incorporation of sodium ions. In particular the outer surface is likely to be rich in sodium and it may have some amorphous character<sup>6</sup> that gives it increased solubility.

All the fully crystalline products contained substantial quantities of sodium ions. The number of sodium atoms per unit cell was found to be linearly dependent on the cation fraction,  $2x/(2 + 2x)$ , in the reaction mixture (Figure 2). The

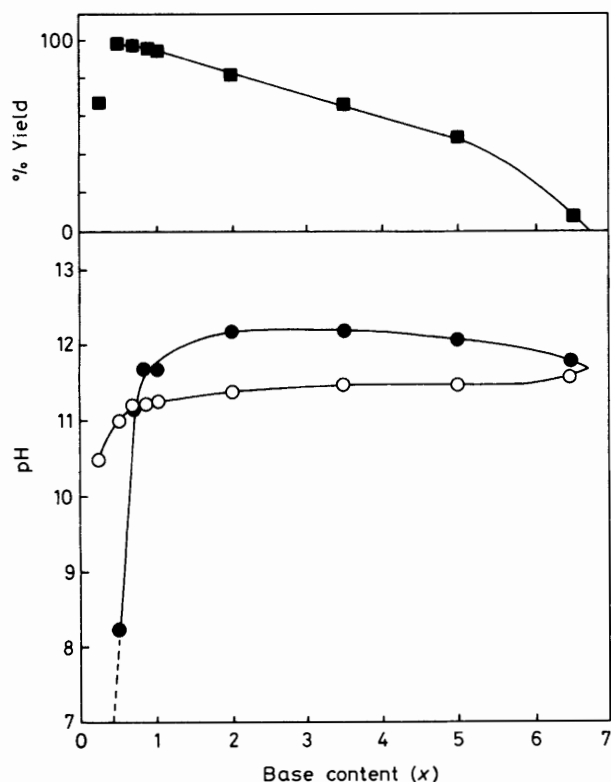


Figure 1. % Yield based on  $\text{SiO}_2$  (■) and pH of initial gel (○) and final mother liquor (●) as a function of base content,  $x$ .

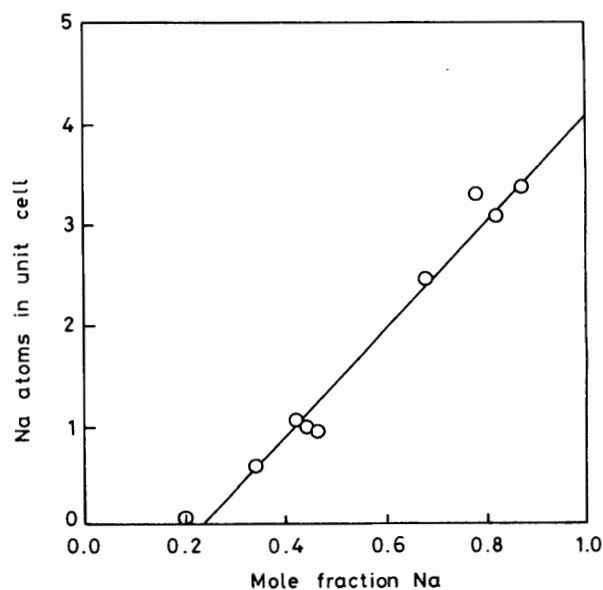


Figure 2. Number of sodium atoms in unit cell as a function of mole fraction  $2x/(2x + 2)$  of sodium ions in reaction mixture.

minimum cation fraction for incorporation of sodium into the molecular sieve ( $0.24 \pm 0.08$ ) is within experimental error of the value (0.294) required to provide sufficient base for complete crystallisation of all the silica as  $4\text{TPAOH } 96\text{SiO}_2$ . Extrapolation of the straight line to a sodium cation fraction of unity gives the maximum number of sodium ions per unit cell that could be incorporated from these reaction mixtures. The value ( $4.1 \pm 0.5$ ) suggests that the limiting unit cell composition of (Na, TPA) silicalite-1 in this system is  $4\text{NaOH } 4\text{TPAOH } 96\text{SiO}_2$ .

The dominant feature of this crystallisation and no doubt that of related zeolitic materials with very low aluminium contents is base occlusion. It is not possible to tell from the present measurements whether the charge on the occluded cations is balanced by hydroxide ions or broken siloxane bonds, though it seems likely that both are present and

probably in equilibrium with each other. If the negative charge is present as a broken siloxane bond the sodium ions should be exchangeable and thus these materials may be ion exchangers despite the absence of aluminium in the frameworks.

S. G. F. thanks the S.E.R.C. for a studentship.

*Received, 15th December 1983; Com. 1628*

### References

- 1 J. L. Casci and B. M. Lowe, *Zeolites*, 1983, **3**, 186.
  - 2 B. M. Lowe, *Zeolites*, 1983, **3**, 300.
  - 3 E. M. Flanigen, J. M. Bennett, R. W. Grose, J. P. Cohen, R. L. Patton, R. M. Kirchner, and J. V. Smith, *Nature*, 1978, **271**, 512.
  - 4 R. W. Grose and E. M. Flanigen, U.S.P. 4061724.
  - 5 F. G. Dwyer and E. E. Jenkins, U.S.P. 3941871.
  - 6 R. K. Iler, 'The Chemistry of Silica,' Wiley, New York, 1979, p. 30.
-