Crystallisation of (Hexane-1,6-diamine)–Silicalite-1

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(Hexane-1,6-diamine)–silicalite-1 is crystallised at 100 °C from the reaction mixture $10M_2O/60SiO_2/10H_2N[CH_2]_6NH_2/3000H_2O$ (M = K or Rb); quaternary ammonium ions are not essential for the crystallisation of the silicalite-1 framework.

The silica molecular sieve, silicalite-1, is prepared as its organic-filled precursor by hydrothermal crystallisation from reaction mixtures that contain tetrapropylammonium 'template' ions.[1—3] It has the same framework structure (*MFI*) as the high-silica zeolite ZSM-5, but whereas a wide range of organic void fillers can be used in the synthesis of the zeolite[4,5] only quaternary ammonium ions have proved effective for the molecular sieve. However it has recently been reported[6] that silicalite-1 can be crystallised at elevated temperatures (160—200 °C) from reaction mixtures that contain void-filling amines, such as pyrrolidine, provided these mixtures also contain some boric acid. We now report that, even in the absence of boron, silicalite-1 can be crystallised from reaction mixtures that contain hexane-1,6-diamine. It is well known that this amine is a good void filler for ZSM-5,[4,7,8] but the essential conditions for its effective use in aluminium-free systems have not been reported.

Hydrothermal crystallisation of the reaction mixture $10M_2O/60SiO_2/10H_2N[CH_2]_6NH_2/3000H_2O$ (M = Na, K, or Rb) was carried out in stirred autoclaves by our usual procedure.[4] The products and reaction conditions are summarised in Table 1. At 100 °C the potassium and rubidium systems both give highly crystalline (hexane-1,6-diamine)–silicalite-1 free from amorphous material. The *X*-ray diffraction pattern of the product was closely similar to that for orthorhombic tetrapropylammonium–silicalite-1, but was transformed to that for monoclinic silicalite-1 on calcination at 800 °C for 19 h. Similar behaviour has been observed for tetrapropylammonium–silicalite-1.[9] Thermal analysis in flowing air showed that most of the hexane-1,6-diamine was lost from the framework over the temperature range 300—600 °C. The total weight loss above 200 °C corresponded to a unit cell composition of $(H_2N[CH_2]_6NH_2)_{7.0}(SiO_2)_{96}$. Chemical analysis of the calcined material gave $(Na_2O)_{0.015}(K_2O)_{0.33}(Al_2O_3)_{0.14}(SiO_2)_{96}$.

Table 1. Crystallisation of $10M_2O/60SiO_2/10H_2N[CH_2]_6NH_2/3000H_2O$: conditions[a] and products.[b]

M	T/°C	t/d	Products
Na	100	13	ZSM-48 (medium) + silicalite-1 (medium)
K	100	11	Silicalite-1[c]
	120	12	ZSM-48 (major) + silicalite-1 (medium) + kenyaite (trace)
	150	7	α-quartz
Rb	100	9	Silicalite-1[c]

[a] T = crystallisation temperature; t = duration of reaction (days). [b] The terms in parentheses are a rough guide to the amount of each crystalline material present in the mixtures; this was estimated from peak heights in the *X*-ray powder diffraction pattern. [c] Diffraction pattern contained an additional very small peak at 2θ 6°, d = 14.73Å, ascribed to a minute trace of an unidentified impurity.

The formation of (hexane-1,6-diamine)–silicalite-1 is critically dependent on the amount of potassium hydroxide present; a reduction from $10K_2O$ to $7.5K_2O$ at 100 °C led to the simultaneous crystallisation of (hexane-1,6-diamine)–silicalite-1 and (hexane-1,6-diamine)–ZSM-48. A small amount of an unidentified impurity (strongest diffraction line at 2θ 6°, d = 14.73 Å), which decomposed to amorphous material on calcination at 800 °C, was also formed.

With increasing temperature denser phases are formed; silicalite-1 (three-dimensional channel system) gives way to ZSM-48 (one-dimensional channel system) at 120 °C, which in turn gives way to α-quartz at 150 °C. This trend is similar to that recently reported[6] and is in line with work on the synthesis of aluminium-rich zeolites in which open framework structures are favoured at lower temperatures.[10] The trend has both kinetic and thermodynamic origins. Even at 150 °C a minor amount of silicalite-1 (along with a major amount of kenyaite) is formed initially, but this is rapidly transformed into the dense stable phase α-quartz. If tetrapropylammonium salts were used instead of hexane-1,6-diamine in any of the reactions investigated, pure tetrapropylammonium–silicalite-1 would be formed and there would be no tendency to over-run to dense phases. Hexane-1,6-diamine is much less effective than the tetrapropylammonium ion in stabilising the *MFI* structure, and hence unless it is used at low temperatures there is a strong tendency for the silicalite-1 to be transformed into more thermodynamically stable materials. Only when there is an electrostatic contribution to the stabilisation energy, *i.e.* when the framework contains amounts of aluminium or boron beyond typical impurity levels, is hexane-1,6-diamine an effective void filler at higher temperatures.

There is no reason to believe that hexane-1,6-diamine is the perfect void filler for silicalite-1; it could well be that, used under similar conditions, some amines will be more effective, whereas others might lead to the crystallisation of different open-framework silica molecular sieves.

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