

Spontaneous nucleation and growth of pure silica zeolite- β free of connectivity defects

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A microporous SiO₂ material isomorphous to zeolite- β showing an enhanced crystallinity and thermal stability due to the absence of connectivity defects, spontaneously nucleates and grows in a hydrothermal system containing tetraethylammonium and fluoride ions at near neutral pH.

Zeolite- β is the only high-silica zeolite possessing a three-dimensional system of large rings (rings of 12 oxygen atoms as the minimum constricting apertures). This gives zeolite- β interesting potential applications in acid-catalysed reactions where high thermal and hydrothermal stability and low steric restrictions can be of paramount importance. The successful synthesis of Ti- β ,¹ an aluminosilicate material with Ti incorporated into the framework, allowed also the use of this large-pore zeolite in selective oxidation reactions. Another reason for the interest in zeolite- β is the possibility of synthesizing a chiral, enantiomerically pure zeolite and the potential applications of such a catalyst in enantioselective reactions. Zeolite- β is an intergrowth of two (or three) polymorphs,^{2,3} one of them being the only known real zeolite structure showing chirality.

On the other hand, synthesis efforts to widen the range of Si/Al molar ratios of this zeolite beyond the limits established in the original patent (Si/Al = 5–100)⁴ had limited success. However, it was very recently reported the synthesis of a so-called pure silica zeolite- β by using dimethyldibenzylammonium as the structure-directing agent.⁵ Unfortunately, this method requires the use of deboronated borosilicate zeolite- β as seeds. Similarly, we were able to synthesize zeolite Ti- β with tetraethylammonium in basic media with Si/Al ratios up to 5000 and above in the final material, but this required the use of dealuminated zeolite- β as seeds.⁶ Since no unseeded synthesis was reported the common belief was that pure silica zeolite- β can grow but it can not nucleate spontaneously in the absence of Al or another element with an oxidation state of +3.⁷ On the other side, all these very high silica zeolite- β and Ti- β synthesized in OH⁻ media were plenty of defects of connectivity (Si-O⁻ or Si-OH groups).^{5,6} On this basis those materials are better described as (HO)_xSiO_{2-x/2} (with x typically >0.16)⁵ rather than as true SiO₂ materials. The presence of connectivity defects can affect the sorption and hydrophilic/hydrophobic properties of zeolites while usually causing a relatively poor thermal stability. Now, we present for the first time the unseeded synthesis of pure silica zeolite- β and show that this material is highly hydrophobic and presents a very high thermal stability.⁸ This is mainly due to the almost complete absence of Si-O⁻ defect groups, as NEt₄⁺ cations are counterbalanced by occluded F⁻.

Pure SiO₂ zeolite- β was synthesized as follows: 43.62 g of tetraethylammonium hydroxide (35% aqueous solution, Aldrich) and 6.21 g of deionized water were mixed in a plastic vessel. Then tetraethylorthosilicate (Merck) was added and the mixture stirred at 25 °C for 6.5 h allowing evaporation of ethanol. To the transparent clear solution obtained 4.32 g of HF (48% aqueous solution) were added. A white solid was formed, which is transferred to Teflon-lined stainless-steel autoclaves and heated to 413 K while being rotated at 60 rpm. The final composition of the mixture, considering the water lost during ethanol evaporation, is 0.54NEt₄OH : 0.54HF : SiO₂ : 7.25H₂O.

After 39 h at the crystallization temperature, the autoclaves are quenched, the contents filtered and the solid washed with deionized water. The pH of the mother-liquor is 9. Around 26.5 g of solid per 100 g of the initial gel were obtained (taking into account a 18.38% mass loss upon calcination at 900 °C, this amounts to ca. 110% conversion of the silica into zeolite). The powder X-ray diffraction pattern (Cu-K α radiation, Philips PW1820) indicates the solid is a highly crystalline zeolite- β (Fig. 1). When the area under the main peak is compared to the standard highly crystalline zeolite- β synthesized in alkaline media, a 100% crystallinity is found for the pure silica sample. This is most probably due to the absence of connectivity defects in the material synthesized with HF and the presence of a great concentration of these defects in the conventional samples synthesized in basic media (these samples do not contain amorphous material detectable by SEM). Pure silica- β shows a much better resolution of the diffraction peaks and this is probably a consequence not only of its large average crystal size (0.5–5 μ m well faceted truncated square bipyramids, SEM) but also of its defect-free nature (see below). Features appearing in the XRD pattern calculated using the proposed faulted model,² which usually are not well resolved in the experimental patterns, are clearly distinguished in the pure silica material. Interestingly, the shoulder at the low-angle side in the first low-angle peak suggests in this material the stacking probability (as defined in ref. 2) is lower than the usual 0.6 value, *i.e.* this material is nearer to polymorph A than to polymorph B (compare inset in Fig. 1 with Fig. 18 of ref. 2).

It is interesting to point out that, for pure silica compositions worked out at high pH, tetraethylammonium has been reported to direct the crystallization towards the formation of MTW and MFI zeolites, and that even in the presence of deboronated zeolite- β seeds, MTW, MFI and cristobalite or magadiite impurities appear.⁵ Under the conditions reported here no impurities at all appeared and the synthesis was perfectly reproduced several times. Furthermore, porosil zeolite- β is stable for at least 5 additional days of heating in the crystallization medium. The reasons for the high selectivity of

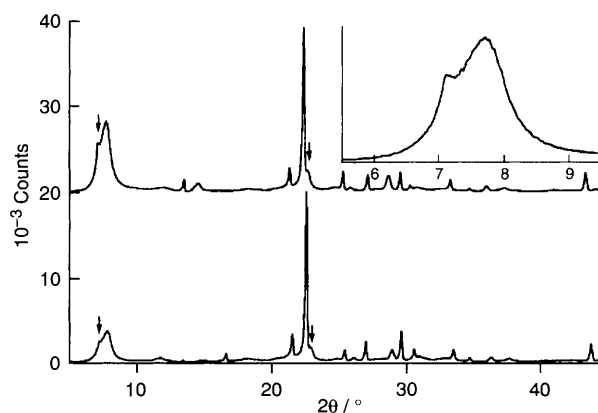


Fig. 1 X-Ray diffraction patterns of pure SiO₂ zeolite- β as-made (bottom) and calcined at 853 K (top and inset)

the reaction media reported here towards the crystallization of pure silica zeolite- β remain a matter for further investigation.

No Al was detected by atomic absorption ($\text{Si}/\text{Al} > 80\,000$). Calcination at 853 K allows removal of the organic cations and F^- anions yielding a pure SiO_2 framework. Calcination up to 1273 K does not result in a loss of crystallinity, while conventional zeolite- β is destroyed. This is again probably due to the absence of connectivity defects. The unit-cell parameters and volume of the calcined sample were refined by a least-squares procedure [tetragonal polymorph: $a = 12.501(2)$, $c = 26.274(6)$ Å, $U = 4106$ Å³; monoclinic polymorph: $a = 12.4669(8)$, $b = 12.456(1)$, $c = 27.625(2)$ Å, $\beta = 107.52(1)^\circ$, $U = 4091$ Å³] showing a significant contraction with respect to aluminosilicate samples, due to the shorter Si–O distance compared to the Al–O distance. The micropore volume of calcined SiO_2 - β is 0.22 cm³ g⁻¹, determined at $P/P_0 = 0.3$ by N_2 adsorption at 77 K.

The absence of connectivity defects in pure SiO_2 - β can be ascertained by solid-state ²⁹Si MAS NMR spectroscopy (Fig. 2). Only Si(4Si) resonances appear. The small resonance at δ ca. -109.4 is not due to Si(3Si, 1 OH) (*i.e.* not due to connectivity defects) because it appears at a field 4 ppm higher than the known range for Si Q³. Furthermore, no signal at all was observed in the ²⁹Si CP MAS NMR spectrum (contact times: 500, 1500 and 3000 μs). Thus, all the resonances correspond to Si(4Si) species and their chemical inequivalence arises from their occupancy of different crystallographic tetrahedral sites. Resolution of crystallographic sites in this spectrum is very similar to that reported by Fyfe *et al.* for a zeolite- β highly dealuminated by post-synthesis SiCl_4 treatment at high temperature.⁹ However, we found two additional Si(4Si) sites (δ ca. -109.4 , -116.1). This suggests that there are subtle differences between the as-made SiO_2 sample and the sample obtained by dealumination. Comparison of the experimental spectrum and that calculated from crystallographic data for polymorphs A, B, C described by Newsam *et al.*² and polymorph C described by Higgins *et al.*³ using the experimental equation reported by Thomas *et al.*¹⁰ (not shown)

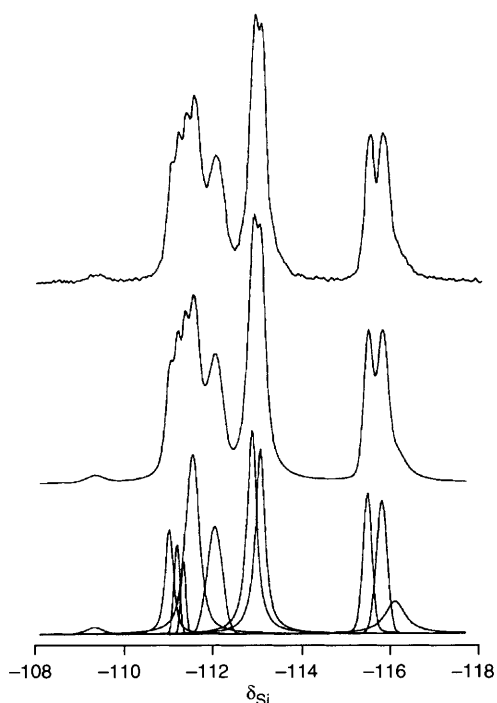


Fig. 2 ²⁹Si MAS NMR spectra of calcined pure silica zeolite- β . Top to bottom: experimental, simulated and deconvoluted components (spectrum recorded at 5 kHz spinning rate, 3500 scans, 20 s recycle delay, 79.4586 MHz, $3\pi/8$ rad, 3 μs pulse length, Varian VXR400SWB).

suggests polymorph A is predominant in our sample, although at least another polymorph with both smaller and larger Si–O–Si angles must also exist. However, since structural data derived from refinement of powder XRD data are not highly accurate, we cannot draw definitive conclusions on the relative population of different polymorphs from this simulation. Note that the presence of broad and sharp reflections in the X-ray diffraction pattern (Fig. 1) is a clear indication of this material showing stacking faults.

The search for new zeolitic materials with compositions beyond the usual range is a matter of both fundamental and technological interest. In the case of zeolite- β , the conclusion was drawn that Al (or other trivalent element) is necessary for its nucleation to occur. The synthesis reported here shows this is not true. While the effect of HF as a mineralizer is clear, it is not easy to rationalize. The HF method was previously used by other workers in the presence of a different template (diazabicyclooctane plus methylamine)¹¹ but under those conditions seeds were needed in order to get pure zeolite- β and the maximum attainable Si/Al ratio was reduced to 22 (compared to 40⁷ or 100⁴ in NET_4OH media or to infinity in the NET_4F media shown here).

Finally, it was recently shown that there are little differences in energy for pure silica polymorphs of zeolitic or dense nature.¹² Drawing conclusions on the synthesis from these results is not straightforward, since what it is actually synthesized is not the pure silica framework but the composite (SiO_2 framework)/(organic structure-directing agent). However, it can be argued that, if just an adequate stabilization of the framework by the organic agent is provided, the synthesis of pure silica microporous materials is a matter of finding the kinetic path leading to the desired structure while preventing the crystallization of perhaps slightly more stable phases. In this sense, the spontaneous nucleation and growth of the long-sought pure silica zeolite- β presented here is encouraging, as this is the crystalline SiO_2 material with the lowest framework density (15.5 TO₂ 1000 Å⁻³) ever reported by direct synthesis. The synthesis of other pure silica, low-framework density materials (with FAU structure, for example) can be thus foreseen.

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