ITQ-4: a new large pore microporous polymorph of silica

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A new silica polymorph of zeolitic nature with large pores, a large void volume and essentially no connectivity defects, is prepared by direct hydrothermal synthesis in a fluoride medium.

An infinity of different hypothetical topologies can be built based on TO_4 tetrahedra sharing all their vertices to yield (4;2) three-dimensional nets,[1] and more than a hundred are actually known to occur as silica, aluminosilicate and aluminophosphate materials.[2] Among the pure silica materials the number of actual topologies is relatively small: several dense phases and clathrasils and only a limited number of microporous phases are known. It is notable that, until very recently, only two pure silica polymorphs having 12 membered ring (12MR) large pore structures, ZSM-12[3] and SSZ-24,[4] have been obtained by direct synthesis. This is despite recent calorimetric measurements[5] and theoretical calculations[6] which showed that the enthalpy of formation of microporous or dense pure silica phases relative to that of quartz is very small (below 15 kJ per mol of SiO_2). This result suggests there should be little energetic limitation to the synthesis of pure silica phases of ever decreasing framework density and thus is in contrast with the seeming difficulty to synthesize such phases. Obviously, it is not possible to directly extend these results to the template-mediated synthesis of pure silica phases, since what is actually synthesized is the composite silica framework/templating species. However, it has been suggested that the formation of pure silica phases is geometrically and kinetically, rather than energetically, controlled,[5] implying it is a matter of finding the right templating effect and the right chemical path. We reported recently the first synthesis of a true pure silica polymorph† with a three-dimensional zeolitic channel system of large pores (12MR), which beautifully exemplifies the above statement. In this case, the long-sought pure silica zeolite β spontaneously nucleates and grows free of connectivity defects under hydrothermal conditions, in the presence of both tetraethylammonium cations and F^- anions.[7] Pure silica β is the SiO_2 polymorph with the lowest framework density ever reported by direct synthesis. Rather than on the templating ability of tetraethylammonium, the success of this synthesis relied on the use of fluoride anions at near neutral pH in a dense system (H_2O/SiO_2 *ca.* 7).[8] The use of F^- anions for the synthesis of defect-free pure silica phases was first established by Flanigen and Patton[9] and subsequently developed by others.[10] The results we present here show how this methodology may be extended, revealing its successful application to the synthesis of another new, large pore microporous pure SiO_2 phase containing a large void volume. The synthesis of an increasing number of new microporous pure silica phases using this strategy can be anticipated, with the limits of the method with respect to pore size and void volume still to be established.

The synthesis of the new phase (denoted as ITQ-4, for Instituto de Tecnología Química-4)[11] in its pure SiO_2 form free of connectivity defects was achieved by using *N*-benzylquinuclidinium employing conditions similar to those previously described for pure silica zeolite β.[7] In a typical synthesis 24.59 g of tetraethylorthosilicate were added to 42.46 g of a 1.4×10^{-3} mol g^{-1} solution of *N*-benzylquinuclidinium hydroxide, and the mixture was stirred for 8 h at room temp. allowing evaporation of the ethanol produced. Then, after adding 10.12 g of water lost during the evaporation and 2.46 g of 48 mass% HF and stirring, the mixture was transferred to PTFE lined stainless steel 60 ml autoclaves, which were heated at 150 °C under tumbling (60 rpm) for 12.5 days. The resulting mixture (pH = 8.2) was then filtered and washed with deionized water. A white highly crystalline solid was obtained (15 g solid/100 g of initial reaction mixture, *i.e. ca.* 90% of the silica was recovered in the solid) having a characteristic powder X-ray diffraction (XRD) pattern shown in Fig. 1(*a*). This pattern was indexed as monoclinic with unit-cell dimensions of $a = 18.599(1)$, $b = 13.401(9)$, $c = 7.701(2)$ Å and $\beta = 101.39(1)°$. Chemical analysis reveals, within experimental error, that the sample contains no Al, and further suggests the organic cation to still be intact within the zeolitic channels [Anal. Found: C, 14.83; H, 1.91; N, 1.25. $(C_{14}H_{20}NF)_{2.16}Si_{32}O_{64}$ requires C, 15.12; H, 1.81; N, 1.26%]. Thermogravimetric and difference thermal analyses show no mass loss below 100 °C, indicating the presence of very little or no occluded water, while in the temperature range 200–750 °C there are two overlapping mass loss steps of roughly equal size which amount to about 20% mass, attributable to the oxidation of the template. The experimental chemical composition of $(C_{14}H_{20}NF)_{2.16}Si_{32}O_{64}$ has been calculated for a unit cell containing 32 SiO_2 units (the number of Si atoms per unit cell was derived from the measured void volume fraction and the unit-cell volume). The volume of two template molecules {*ca.* 310 Å^3 per molecule, assuming free rotation of both the quinuclidinium and benzene moieties around the N–C^9 and C^9–C^{10} bonds, respectively, of the *N*-benzyl-1-azoniumbicyclo[2,2,2]octane} per unit cell is in very good agreement with the void volume derived by N_2 adsorption [670 Å^3 (u.c.)$^{-1}$, see below], suggesting that there is a close packing of the organics within the silica framework and that essentially all the void volume accessible to N_2 in the calcined sample is occupied by the *N*-benzylquinuclidinium in the as-made sample. This

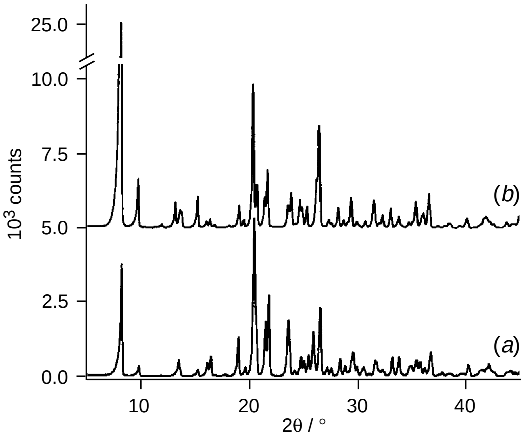

Fig. 1 Powder X-ray diffractograms of (*a*) as prepared ITQ-4 and (*b*) ITQ-4 after calcination at 580 °C for 3 h. The changes to the pattern after calcination are related to a change in the unit-cell dimensions of the detemplated solid. Philips PW1820 diffractometer, Cu-Kα radiation, 0.020° 2θ step size and 0.500 s count time.

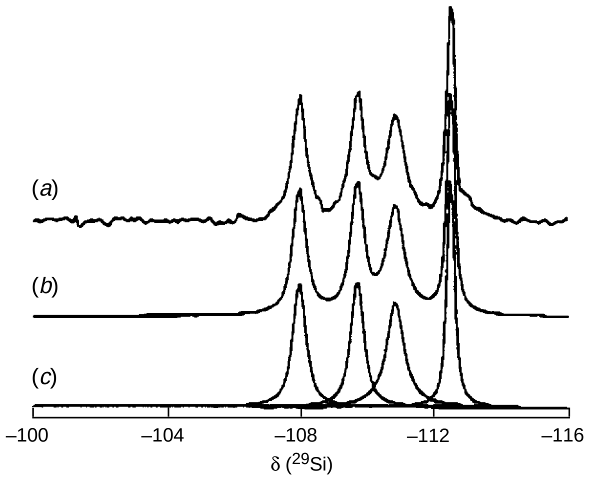

Fig. 2 ^{29}Si MAS NMR spectra of calcined ITQ-4, distinctly showing four resolved Si(4Si) crystallographic sites in the structure of the new pure SiO_2 polymorph: experimental (*a*), simulated (*b*) and deconvoluted components (*c*). Spectrum recorded on a Varian VXR400 SWB at 5 kHz spinning rate, 60 s recycle delay, 79.4586 MHz, 3π/8 rad, 3 μs pulse length, 264 scans.

implies that the void volume accessible to N_2 consists only of rather large cages or channels.

After calcination at 580 °C for 3 h the solid is freed of the organic material with retention of its crystallinity [Fig. 1(*b*)] and symmetry (as deduced from the laboratory XRD data, which were fully indexed with the same symmetry for the as-made and calcined materials). There are however significant changes in peak positions due to changes in the unit-cell parameters [a = 18.619(20), b = 13.478(9), c = 7.625(16) Å, β = 101.947(16)°]. Upon calcination, the unit cell shrinks in the c crystallographic direction, while it expands in the a and b directions, the overall result being a contraction of its volume by a factor of 0.5% (1880.66 and 1871.88 Å^3 for the as-made and calcined samples, respectively). Typically, zeolite frameworks expand upon removal of the organic molecules by calcination, while the effect observed here suggests a tight fit of the template within the zeolitic void volume, with the framework relaxing in the calcined form. No loss of crystallinity was observed after heating ITQ-4 to at least 1273 K. The high thermal stability of this phase is attributed to its pure silica nature and to the absence of Si–O–Si connectivity defects (see below). After calcination, the microporous nature of ITQ-4 was probed by its N_2 adsorption isotherm at 77 K, from which the following adsorption values were derived: microporous volume 0.21 cm^3 g^{-1}, micropore area 415 m^2 g^{-1}, BET surface area 433 m^2 g^{-1}. By adsorption of Ar at 87.3 K and using the Horvath–Kawazoe formalism a pore size of 6.2 Å was calculated suggesting ITQ-4 is a large 12MR pore material.

The true SiO_2 nature of ITQ-4 (*i.e.* a 4-connected three-dimensional net of SiO_4 tetrahedra with no Si–O–Si connectivity defects and no Al) is evidenced by ^{29}Si MAS NMR spectroscopy of calcined pure silica ITQ-4 (Fig. 2). First, and within the limits of detection of this technique, no signals are detected in the region below δ 105, showing the absence of Si(3Si, 1OH) or Si(3Si, 1Al) species. Secondly, the spectrum shows a very high resolution of tetrahedral Si(4Si) sites, directly attributable to the crystallographically distinct Si environments in the structure. Such a high resolution is generally only observed in cases where there is essentially complete absence of Si–OH and Si–O–Al species. In Table 1 a list of the intensities and positions of the four deconvoluted components of the spectrum is given, together with the average Si–O–Si angles calculated using the relationship of Thomas *et al.*[12] for every resolved Si site. The rather small Si–O–Si average angle for every Si site in ITQ-4 (142–150°) is remarkable, the average value (146.5°) being *ca.* 5–10° smaller than the usual T–O–T angles typically found in pure silica zeolites (around 150–155°).

Table 1 Results of the deconvolution of the ^{29}Si MAS NMR spectrum of pure SiO_2 ITQ-4

Signal (δ)	Relative intensity	Average Si–O–Si angle[12]
−107.97	23.8	142.5
−109.71	23.9	145.5
−110.86	27.6	147.5
−112.52	24.8	150.3

Finally, we note that in view of its characteristic XRD pattern, ITQ-4 appears to be related, being probably isomorphous, to a recently described zeolite of unknown structure, SSZ-42,[13] for which no report exists in the literature. The information contained in its original patent suggests this material is a large pore one. Very interestingly, SSZ-42, for which the template employed here can also be used, can not be synthesized in the absence of B atoms in the conditions reported in the patent (OH$^-$ media). Thus, the synthesis reported here, when viewed together with that already reported for pure SiO_2 β,[7] exemplifies how the appropriate synthesis method can help circumvent the apparent difficulty of synthesizing very open pure silica polymorphs, and corroborates the conclusion drawn by other authors concerning the small energetic limitations to the synthesis of large pore pure silica phases.[5]

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Footnotes

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† Phases containing extensive Si–O–Si connectivity defects, frequently encountered in zeolite synthesis, are better formulated as $SiO_{2-x}(OH)_{2x}$, rather than as true pure SiO_2 polymorphs.

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