Synthesis and structure of ITQ-9: a new microporous SiO_2 polymorph

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The new pure silica polymorph ITQ-9 has been synthesised and its structure, comprising medium pore channels and cages, has been solved by direct methods using low resolution powder X ray diffraction data.

Crystalline silica occurs in nature in a small variety of non-porous structural forms. However, it is also possible to synthesise SiO_2 as microporous solids by hydrothermal crystallisation in the presence of organic additives. These additives, which typically remain occluded within the porous silica framework, are called structure directing agents (SDA) and may generally be removed by calcination giving stable, crystalline pure silica polymorphs. A recent viewpoint considers that the role of SDA molecules is to select between different possible silica structures[1] with similar enthalpies of formation.[2] In our opinion, the SDA either kinetically or thermodynamically directs the crystallisation toward a specific phase. When the crystallisation is carried out at near to neutral pH (7–9.5) in the presence of fluoride anions which act as mineralisers, the crystalline silica obtained after calcination generally shows a very high degree of perfection. More specifically, those phases present essentially no Si–O–Si connectivity defects, which are by contrast frequent if the synthesis is carried out in basic medium (with OH^- acting as mineraliser). Owing to the lack of defects the final materials prepared in fluoride aqueous media are very attractive since they show strict hydrophobic properties[3] and a high degree of both short and long range order.[4] We describe here the synthesis of a new crystalline form of SiO_2, denoted ITQ-9 (Instituto de Tecnología Química, no. 9), which possesses a large micropore volume. In addition, we also show that the high degree of crystallographic order presented by this material afforded the resolution of its low symmetry structure by direct methods using low resolution powder X ray diffraction data (PXRD).

Pure silica ITQ-9 has been synthesised using *N,N*-dimethyl-6-azonium-1,3,3-trimethylbicyclo(3.2.1)octane (**I**) as SDA. 24.89 g of tetraethylorthosilicate were hydrolysed in 36.65 g of an aqueous solution of this cation in hydroxide form (1.63 moles per 1000 g of solution) under stirring and allowing evaporation of all the ethanol produced plus 16.7 g water. Then, 2.48 g of HF (48% aq.) were added and the thick paste obtained was homogenised by hand stirring before pouring into Teflon lined stainless steel autoclaves. These were heated at 150 °C under slow rotation (60 rpm). After 16 days of heating the contents were filtered, washed and dried. A highly crystalline solid was obtained and its PXRD pattern was indexed as monoclinic, space group $I2/m$, $I2$ or Im, a = 14.7906, b = 18.1528, c = 7.4547 Å, β = 110.76°. Chemical analysis suggests the chemical formula for as-made ITQ-9 is $[C_{12}H_{24}NF]_2[SiO_2]_{32}$ (based on the unit cell of the calcined material determined in this work, see below) and that the organic SDA is intact within the zeolite.

Calcination in air at 800 °C for 3 hours allows complete removal of the guest species yielding a pure SiO_2 framework with a large micropore volume of 0.21 $cm^3\ g^{-1}$ (determined by the t-plot method from the N_2 adsorption isotherm at 77 K). This framework is essentially free of connectivity defects, as demonstrated by the lack of significant Si(3Si,1OH) resonances near −101 ppm in the ^{29}Si MAS NMR spectrum (Fig. 1, top). The spectrum shows only Si(4Si) resonances in the −107 to −116 ppm chemical shift range. As a consequence of the absence of defects and high short range order there is a high resolution of Si(4Si) sites corresponding to framework Si in at least 6 different crystallographic sites.

After calcination splitting of a number of peaks in the PXRD pattern of ITQ-9 was observed. All the peaks could be indexed as a triclinic cell close to that for the as-prepared material, whilst maintaining the I centering (space group I-1). Direct methods using the Sirpow[5] program with Le Bail[6] extracted intensities from the Mprofil[7] program gave no satisfactory solution (a cell content of 32 SiO_2 derived from the density of 1.662 g cm^{-3} determined by pycnometry was used). We thus decided to use the PXRD data of the as-made sample due to its higher monoclinic symmetry. Le Bail extraction and direct methods were repeated as before using space group $I2/m$ for which a good solution for the framework lacking no Si or O atoms and consisting of a 3D 4-connected net was obtained. Small fragments of organic matter were also found. Hence, the SiO_2 framework obtained for the as-made sample was used, after generation of the additional atomic positions in space group I-1, as a starting model for the Rietveld[8] refinement of the calcined triclinic phase, using conventional laboratory PXRD data in the program GSAS[9] with a manually interpolated background together with a pseudo Voigt[10] function to describe the peak shape. Constraints on the Si–O distances were used in the first stages of the refinement and finally removed before the model was refined to convergence. The crystallographic data are summarised in Table 1 and the final atomic positions are

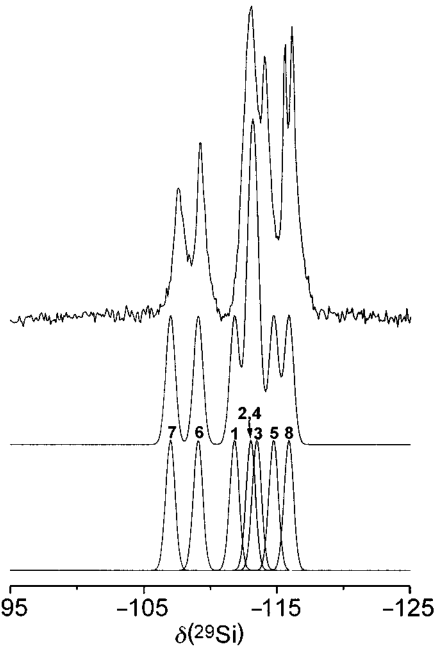

Fig. 1 ^{29}Si MAS NMR (*vs.* TMS) spectrum of calcined pure silica ITQ-9 (top) together with a simulation (middle) obtained by applying the equation of Thomas *et al.*[11] to the average Si–O–Si angles of each Si site in the refined structure (calculated resonances for each individual site are shown at the bottom). Note the absence of Si(3Si,1OH) resonances near −101 ppm and the high resolution of crystallographic sites in the experimental spectrum.

Table 1 Data collection and crystallographic parameters for calcined ITQ-9

Wavelength		Cu-Kα
Temperature/K		298
2θ range/°		5–85 (Range used 15–85)
Step size, 2θ/°		0.01
Count time/s step^{-1}		10 (5–50° 2θ); 40 (50–90° 2θ)
Number of data points		6910
Number of reflections		2527
Number of profile parameters		11
Number of structural parameters		81
Number of constraints		32
Unit cell	a/Å	14.7685(13)
	b/Å	18.1793(17)
	c/Å	7.3823(7)
	α/°	89.1402(21)
	β/°	110.6790(26)
	γ/°	90.945(4)
Space group		I-1
Residuals	R_{exp}	7.45
	R_{wp}	9.57
	R_p	7.72
	R_b	9.16
	χ^2	1.719

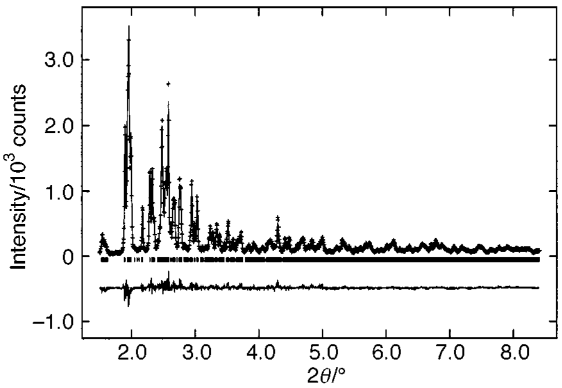

Fig. 2 Rietveld plot for calcined pure SiO_2 ITQ-9: observed data (+), calculated profile (solid line) and difference (lower trace). The tick marks represent the positions of allowed reflections.

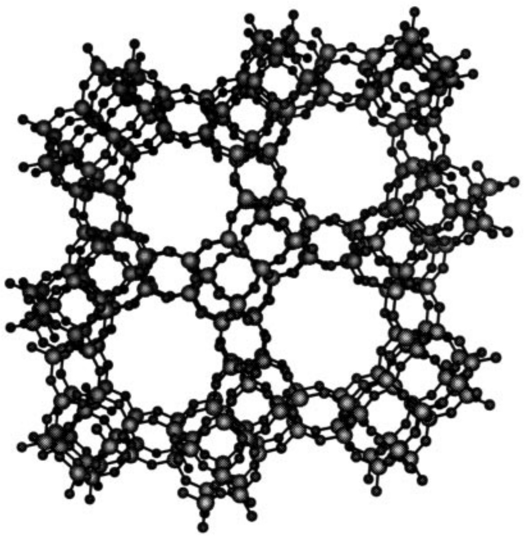

Fig. 3 A perspective view of the framework structure of ITQ-9 down [001], showing the nearly circular one-dimensional 10MR pores (average free diameter ≅ 5.7 Å). Large spheres represent tetrahedral Si, while small spheres are two-coordinated O.

available as Electronic Supplementary Information (http://www.rsc.org/suppdata/cc/1998/xxxx), with the final Rietveld plot depicted in Fig. 2. The average Si–O bond length (1.596 Å) and average O–Si–O and Si–O–Si angles (109.4 and 149.9° respectively) are in excellent accord with those expected for zeolite materials. Moreover, simulation of the ^{29}Si MAS NMR spectrum using the average Si–O–Si angles determined by Rietveld refinement for each Si site and the empirical equation of Thomas *et al.*[11] is in excellent agreement with the experimental spectrum (Fig. 1). Energy minimisation calculations using the GULP code[12] together with the potential model of Saunders *et al.*[13] reveal the symmetry lowering to be favourable by *ca.* 5 kJ mol^{-1}.

A projection of the structure of ITQ-9 is presented in Fig. 3. ITQ-9 is a new pure silica polymorph containing one dimensional sinusoidal pores running along [001] with access through ten membered ring windows (10MR windows). The windows are nearly circular in shape and have an average free diameter of around 5.7 Å (assuming the van der Waals radius of O to be 1.35 Å). The maximum and minimum diameters are 6.0 and 5.4 Å, respectively. Between two adjacent 10MR windows there are wider spaces with approximate free dimensions 10.9 Å × 7.4 Å × 4.7 Å. Thus, the pores in essence may be regarded as a one-dimensional arrangement of cages joined through single 10MR windows. In some directions the separation between adjacent pores is a wall with a single O atom (Fig. 3). This and the presence of cages explains the sizeable micropore volume of ITQ-9 (0.21 cm^3 g^{-1}) which is exceedingly large compared to other one-dimensional 10MR (ZSM-23, 0.04 cm^3 g^{-1}), 12MR (SSZ-24, 0.12 cm^3 g^{-1}) or even 14MR (CIT-5, 0.13 cm^3 g^{-1})[14] zeolites.

Finally, Al can be introduced by direct synthesis into the structure of ITQ-9. The aluminosilicate ITQ-9 presents strong Brønsted acid sites attributed to $[Al(OSi)_4]^-$ framework groups, as revealed by pyridine adsorption and desorption at increasing temperatures monitored by IR spectroscopy. This, together with the large micropore volume of the zeolite, renders ITQ-9 an attractive material for the catalytic transformation of hydrocarbons. Its activity and shape selectivity properties (due to the peculiar pore system encompassing medium sized windows and large cages) are currently under investigation.

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