Synthesis and structure of pure SiO_2 chabazite: the SiO_2 polymorph with the lowest framework density

María-José Díaz-Cabañas, Philip A. Barrett and Miguel A. Camblor*

Instituto de Tecnología Química, Avda. Los Naranjos s/n, 46071 Valencia, Spain. E-mail: macamblo@itq.upv.es

A SiO_2 material with the lowest framework density (15.4 SiO_2 nm^{-3}) and the largest void volume fraction (nearly 50%) ever reported for crystalline silica polymorphs has been synthesised, and its structure solved by direct methods and fully refined using low-resolution powder X-ray diffraction data.

The synthesis of pure silica polymorphs of decreasing density is a scientific challenge which may result in potential applications, including adsorption and separation of organic molecules but also storage of gases such as H_2 and CH_4. Compared to zeolites of the same structure type pure silica polymorphs may in principle offer (1) a larger void space owing to the absence of counter cations in their pores, (2) distinct adsorption properties, characterised by their extreme hydrophobicity,[1] and (3) a far superior thermal stability. Recent calorimetric measurements[2] and theoretical calculations[3] have shown that the enthalpy of formation relative to quartz is very small and increases only slightly with the decreasing framework density (FD, the number of $SiO_{4/2}$ tetrahedra per nm^3). This suggests the synthesis of low-density materials is not thermodynamically hindered and new phases (though normally considered as still metastable with respect to quartz) could be obtained through a kinetic control of the synthesis process. Actually, the synthesis of microporous SiO_2 polymorphs involves a two-step process: the synthesis of a host–guest compound in the presence of a suitable (normally organic) structure-directing agent (SDA), and its calcination to remove the guest organics. Apparently, the use of SDAs affords the required kinetic pathway and/or the additional stabilisation energy that makes the synthesis feasible. However, until recently only silica phases with a relatively high framework density (above 17 $SiO_{4/2}$ nm^{-3}) have been obtained. We have recently found that a modification of a known method for the synthesis of pure silica materials offers new opportunities for decreasing the framework density of the phases obtained.[4] We illustrate here the success of this strategy which has now afforded the synthesis of a new pure silica polymorph isostructural with zeolite chabazite having the lowest ever reported framework density amongst these materials, 15.4 SiO_2 nm^{-3} (14.6 T nm^{-3} for the type material, structure code CHA).[5]

Pure silica chabazite was synthesised hydrothermally using *N*,*N*,*N*-trimethyladamantammonium (TMAda$^+$) in hydroxide form as the structure-directing agent at near to neutral pH in the presence of fluoride. In a typical synthesis 13.00 g of tetraethylorthosilicate were hydrolysed in 31.18 g of a 1.0 M TMAdaOH aqueous solution and the mixture was stirred to allow the ethanol and water to evaporate to a final H_2O/SiO_2 molar ratio of 3.0. Then, 1.33 g of HF (aq., 46.9%) were added and the mixture, which was homogenised by hand, was transferred to Teflon lined stainless steel 60 ml autoclaves. The autoclaves were heated at 150 °C whilst rotated at 60 rpm. After 40 h crystallisation time (pH = 8.5) the solid product was collected, washed and dried, and recognised as chabazite by powder X-ray diffraction (XRD). Its chemical analysis indicates a composition close to $[C_{13}H_{24}NF_{0.5}]_3[Si_{36}O_{72}(OH)_{1.5}]$ [Anal. Found: C, 17.49; H, 2.98; N, 1.56; F, 1.06. The above composition requires: C, 16.78; H, 2.60; N, 1.51; F, 1.02%]. A charge imbalance between F$^-$ and TMAda$^+$ suggests the presence of connectivity defects in this material (see below), and to maintain electrical neutrality we have included 1.5 OH$^-$ per uc in the above idealised composition.

It is interesting that an aluminosilicate isostructural to chabazite (denoted as SSZ-13) may be prepared using the same structure-directing agent in OH$^-$ medium.[6] However, it appears that in the absence of F$^-$ in alkaline medium aluminium is needed for the synthesis of SSZ-13 to succeed.[6] From our experience in OH$^-$ medium using TMAda$^+$ as the structure directing agent an increase in the Si/Al ratio above 50 favours the crystallisation of either ITQ-1[7] or SSZ-23 (depending on the alkali metal cation present) while higher aluminium contents favours SSZ-13 with the CHA topology.[8]

Thermogravimetric analysis in air (10 °C min^{-1}) shows no weight losses below 260 °C, suggesting no water is occluded as a guest in this material, as expected for a pure silica host. The organics and fluorine are removed in the range 300–650 °C through two overlapping exothermic processes (the first centred at 450 °C). Calcination at 580 °C for 3 h is required to prepare the pure silica host, whose adsorption capacity is exceptionally high. From N_2 adsorption experiments at 77 K a micropore volume of 0.30 cm g^{-1} (calculated by the *t*-plot method or by the amount of adsorbed N_2 at any relative pressure between 0.1 and 0.9), a surface area of 602 m^2 g^{-1} (BET method) and a micropore area of 594 m^2 g^{-1} were calculated. The micropore volume of silica chabazite is by far the largest ever reported for a crystalline pure silica polymorph and exceeds by over 30% those of the beta, ITQ-3 and ITQ-4 materials (0.22, 0.23 and 0.22 cm^3 g^{-1} respectively). The void volume fraction of silica Chabazite is almost 50% (0.46 cm^3 cm^{-3}).

The ^{29}Si MAS NMR spectrum of calcined pure silica CHA (Fig. 1) shows two bands at δ −101.4 and −111.4. The first is assigned to $Si(OSi)_3OH$ defect groups and the second to $Si(OSi)_4$ species. Their relative intensities allow us to quantify the amount of defects in pure silica CHA and shows that an appropriate formulation for this material is $[Si_{36}O_{70.5}(OH)_{2.9}]$. The number of defect groups is relatively small compared to silica materials synthesised in OH$^-$ medium, where the Si–OH concentration is typically about four times larger than the

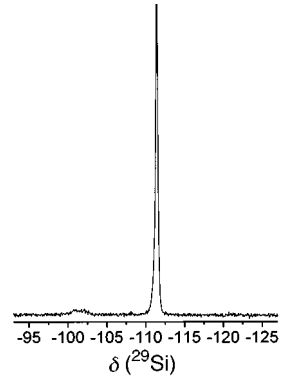

Fig. 1 ^{29}Si MAS NMR spectrum of calcined pure silica chabazite (reference $SiMe_4$ = 0)

Table 1 Data collection and crystallographic parameters for calcined pure silica chabazite

Wavelength		Cu-Kα (graphite monochromated)
Profile range (2θ/°)		5–100
Step size/°		0.01
Step count time/s		2 (5–40° 2θ); 4 (40–100° 2θ)
Number of data points		7740
Number of reflections		609
Profile range used (2θ/°)		22–100
Number of profile parameters		8
Number of structural parameters		14
Number of constraints		0
Unit cell	a/Å	13.52923(8)
	c/Å	14.74828(13)
Space group		$R\bar{3}m$ (no. 166)
Residuals	R_{exp}	7.76
	R_p	8.66
	R_{wp}	11.18
	χ^2	2.083
	R_b	3.96

Table 2 Fractional coordinates and thermal parameters from Rietveld refinement of the pure silica chabasite with esds in parentheses

Atom	x	y	z	U_{ISO}/Å^2
Si(1)	0.22862(10)	0.00002(12)	0.10389(7)	0.0313(7)
O(1)	0.11978(11)	−0.11978(11)	0.12991(18)	0.0308(11)
O(2)	0.33333	0.01978(20)	0.16667	0.0315(10)
O(3)	0.19744(24)	0.09872(12)	0.12173(21)	0.0354(10)
O(4)	0.26344(19)	0	0	0.0335(10)

amount of occluded cations[9] (this would lead in this case to over 30% Si–OH defects with respect to total Si sites). However, it is noticeable that this defect concentration is much larger than expected for a silica material synthesised at near neutral pH in the presence of fluoride.[10] In view of a plausible control of the defect concentration by the synthesis pH and the pK_a of the condensing silicate species,[11] we have tried to reduce the defect concentration of this material by further decreasing the synthesis pH, but with no success. We are currently trying to understand the unexpected behaviour of this system.

The *Si*$(OSi)_4$ resonance in Fig. 1 is noticeable because of its sharpness (26 Hz), which is probably due to a combination of the absence of Al substitution for Si, the presence of a single Si site in the structure (see below) and the relatively low concentration of defects. We have calculated an average Si–O–Si angle of 148.4° for CHA by applying the equation of Thomas *et al.*[12] to the chemical shift of the *Si*$(OSi)_4$ resonance. This is in excellent agreement with the value obtained by Rietveld refinement (148.0°, see below).

Powder X-ray diffraction (XRD) techniques were used to examine the new pure silica Chabazite material. Laboratory Cu-Kα XRD data were recorded on a freshly calcined sample of the title compound. Inspection of the diffraction pattern and refinement of the unit cell parameters taken from Smith *et al.*[13] verified the phase purity and rhombohedral symmetry (space group $R\bar{3}m$). The high crystallinity of the material after calcination enabled the structure to be solved routinely by direct methods in the program Sirpow[14] using Le Bail[15] extracted intensities from the Mprofil[16] program suite. Subsequent Rietveld[17] refinement of the model produced from direct methods was undertaken in the program GSAS[18] using a manually interpolated background together with a pseudo-Voigt[19] function to describe the peak shape. The refinement proceeded smoothly with no constraints used. The crystallographic data are summarised in Table 1, the final atomic positions in Table 2 with the final Rietveld plot depicted in Fig. 2. The average Si–O bond length (1.603 Å) and average O–Si–O and Si–O–Si angles (109.47 and 148.0°, respectively) are in excellent accord with those expected for zeolite materials. These refinement results clearly verify the formation of a highly crystalline chabazitic material.

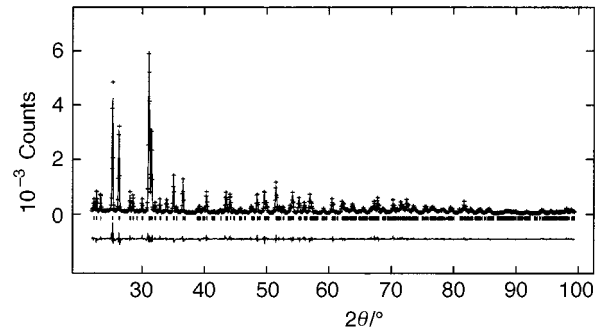

Fig. 2 Rietveld plot for the title compound, observed (+), calculated (solid line) and the difference (lower trace). The tick marks represent the positions of allowed reflections.

The authors greatly acknowledge financial support by the Spanish CICYT (project MAT97-0723). P. A. B. is grateful to the European Union for a postdoctoral fellowship.

Notes and References

1 T. Blasco, M. A. Camblor, A. Corma, P. Esteve, J. M. Guil, A. Martínez, J. A. Perdigón-Melón and S. Valencia, *J. Phys. Chem. A*, 1998, **102**, 75.
2 I. Petrovic, A. Navrotsky, M. E. Davis and S. I. Zones, *Chem. Mater.*, 1993, **5**, 1805.
3 N. J. Henson, A. K. Cheetham and J. D. Gale, *Chem. Mater.*, 1994, **6**, 1647.
4 M. A. Camblor, A. Corma and S. Valencia, *Chem. Commun.*, 1996, 2365; M. A. Camblor, A. Corma and L. A. Villaescusa, *Chem. Commun.*, 1997, 749; M. A. Camblor, A. Corma, P. Lightfoot, L. A. Villaescusa and P. A. Wright, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2659.
5 W. M. Meier, D. H. Olson and Ch. Baerlocher, *Atlas of Zeolite Structure Types*, Elsevier, Amsterdam, 4th edn., 1996.
6 S. I. Zones, R. A. Van Nordstrand, D. S. Santilli, D. M. Wilson, L. Yuen and L. D. Scampavia, *Stud. Surf. Sci. Catal.*, 1989, **49**, 299.
7 M. A. Camblor, C. Corell, A. Corma, M. J. Díaz-Cabañas, S. Nicolopoulos, J. M. González-Calbet and M. Vallet-Regí, *Chem. Mater.*, 1996, **8**, 2415; M. A. Camblor, A. Corma, M. J. Díaz-Cabañas and Ch. Baerlocher, *J.Phys. Chem. B*, 1998, **102**, 44.
8 C. Corell, Ph.D. Thesis, Universidad Politénica de Valencia, 1997.
9 H. Koller, R. F. Lobo, S. L. Burkett and M. E. Davis, *J. Phys. Chem.*, 1995, **99**, 12 588.
10 J. M. Chezeau, L. Delmotte, J. L. Guth and M. Soulard, *Zeolites*, 1989, **9**, 78.
11 P. A. Barrett, M. A. Camblor, A. Corma, R. H. Jones and L. A. Villaescusa, *J. Phys. Chem.*, 1998, **102**, 4147.
12 J. M. Thomas, J. Klinowski, S. Ramdas, B. K. Hunter and D. T. B. Tennakoon, *Chem. Phys. Lett.*, 1983, **102**, 158.
13 L. J. Smith, A. Davidson and A. K. Cheetham, *Catal. Lett.*, 1997, **49**, 142.
14 A. Atomare, C. Burla, C. Cascarano, C. Cascarino, C. Giacovazzo, A. Gualiardi, G. Polidori and R. M. Canalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
15 A. Le Bail, *Mater. Res. Bull.*, 1988, **23**, 447.
16 A. D. Murray and A. N. Fitch, Mprofil program for Le Bail decomposition and profile refinement, 1990.
17 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65.
18 A. Larson and R. B. Von Dreele, GSAS Manual, Los Alamos Report No. LA-UR-86-748, 1986.
19 J. B. Hastings, W. Thomlinson and D. E. Cox, *J. Appl. Crystallogr.*, 1984, **17**, 85.

Received in Bath, UK, 20th June 1998; 8/04800B