Structure of ITQ-4, a New Pure Silica Polymorph Containing Large Pores and a Large Void Volume

P. A. Barrett,[†] M. A. Camblor,*[,†] A. Corma,[†]
R. H. Jones,[‡] and L. A. Villaescusa[†]

Instituto de Tecnología Química, CSIC-UPV
Universidad Politécnica de Valencia
Avda. Los Naranjos s/n, 46071 Valencia, Spain, and
Department of Chemistry, University of Keele
Keele, Staffordshire, ST5 5BG UK

Received March 27, 1997
Revised Manuscript Received June 9, 1997

Zeolites are microporous solids that find a wide range of commercial applications in catalytic, adsorption and separation processes.[1] Their crystalline structures comprise large voids, channels, and cavities, the exact nature of which are central to determining their applications. However, the structural elucidation of zeolites is frequently hindered by the well-known difficulty to synthesize single crystals of suitable size and quality for conventional 4-circle diffractometry and by a considerable degree of structural and hence crystallographic disorder caused by the presence of randomly distributed connectivity defects and/or Al atoms replacing a fraction of the framework Si. As a direct consequence of these synthetic shortfalls, there is commonly a need to employ a combination of techniques, such as synchrotron based powder X-ray diffraction, high-resolution electron microscopy, high-resolution ^{29}Si MAS NMR, and electron diffraction to obtain the required level of structural information. Here we report the straightforward ab initio structure determination from powder diffraction data of a new zeolite having a comparatively low symmetry. This was achieved in part by synthesizing this large pore pure silica polymorph free of "defects" (Al or Si−OH) thereby producing a very high degree of crystallographic order. This new material, denoted ITQ-4,[2,3] contains a sinusoidal large pore channel and its void volume (0.21 cm^3/g) is only surpassed by pure silica Beta[4] among the known pure silica polymorphs. In its Al-containing form the material shows very strong Brønsted acidity and is a promising catalyst for the hydroisomerization of short chain *n*-alkanes and for the re-forming of C_7−C_{10} normal paraffins.[5] The recently patented aluminosilicates SSZ-42[6] and MCM-58[7] possess the same topology as ITQ-4, for which the structure code IFR has been assigned.

Pure silica ITQ-4 was synthesized hydrothermally from a starting mixture of composition SiO_2:0.50 $C_{14}H_{20}N^+$ OH^-:0.50 HF:15 H_2O, heated for 12.5 days at 150 °C in Teflon-lined stainless steel autoclaves rotated at 60 rpm. The organic cation in the above composition is the *N*-benzyl-1-azoniumbicyclo[2,2,2]-octane and is used as the structure directing agent or template allowing the crystallization of ITQ-4. The fluoride anions are used as mineralizing agents, i.e., as catalysts for the breaking and formation of Si−O−Si bonds, and they subsequently act also as counterions for the organic cations in the crystallized material. Without F^- anions, Si−O^- connectivity defects would be necessary to counterbalance for the organic cations occluded in a pure silica framework. The as-made microcrystalline powder was calcined at 650 °C for 3 h to remove the organic cation and F^- anion occluded into its void volume during the crystallization. After this process, the pure SiO_2 polymorph is obtained, and its microporous nature is clearly evidenced by N_2 adsorption, yielding a measured micropore volume of 0.21 cm^3/g.

Preliminary results[2] from laboratory data indicated that calcined ITQ-4 is monoclinic, with cell parameters $a = 18.6$ Å, $b = 13.5$ Å, $c = 7.6$ Å, $\beta = 101.95°$ (Philips PW1820 diffractometer, Cu Kα radiation). The number of Si atoms in the unit cell was estimated to be 32 from the measured void volume fraction and the unit-cell volume. High-resolution solid-state ^{29}Si MAS NMR spectroscopy showed four different Si(4Si) environments, all of them with precisely the same intensity.

High-resolution X-ray powder diffraction data were subsequently collected on station 2.3 of the Daresbury synchrotron radiation source using a wavelength of 1.399 96 Å, a step increment of 0.01°, and a time per step of 2 s for data up to 33.6° 2θ and 6 s for data from 33.6 to 85° 2θ. The systematic absences were consistent with an I-centered space group. A model independent fit was then carried out using a Le-Bail decomposition method,[8,9] which yielded 951 independent reflections. These data were used to solve the structure using the direct methods program SIRPOW[10] which gave the positions of the framework atoms in space group $I2/m$, with four Si crystallographic sites in the asymmetric unit, consistent with the ^{29}Si MAS NMR data. These were input as starting model and refined by the Rietveld profile method[11] using the GSAS[12] suite of programs without imposition of constraints, except that in the final stages of the refinement a common isotropic temperature factor was assigned to the oxygen atoms. During the course of the refinement it was necessary to introduce a parameter to account for preferred orientation of the elongated crystallites in the powder and exclude the reflection with the lowest 2θ value. The model rapidly converged to the residuals reported in Table 1.[12] The final cell parameters are $a = 18.65243(13)$, $b = 13.49597(8)$, $c = 7.63109(6)$ Å, $\beta = 101.9781(5)°$. A plot of the observed, calculated, and difference profiles is given in Figure 1. Final fractional atomic coordinates derived from the Rietveld refinement are listed in Table 2. The value of the individual Si−O bond

---

[†] Instituto de Tecnología Química.

[‡] University of Keele.

(1) Kühl, G. H.; Kresge, C. T. *Kirk Othmer Encycl. Chem. Technol.* **1995**, *16*, 888.

(2) Camblor, M. A.; Corma, A.; Villaescusa, L. A. *Chem. Commun.* **1997**, 749.

(3) Villaescusa, L. A.; Camblor, M. A.; Corma, A. Spanish Patent, P9602685, 1996.

(4) Camblor, M. A.; Corma, A.; Valencia, S. *Chem. Commun.* **1996**, 2365−2366.

(5) Corma, A.; et al., manuscript in preparation.

(6) Zones, S. I.; Rainis, A. PCT/US95/01412, 1995.

(7) Valyocsik, E. W. U.S. Patent 5,437,855, 1995.

(8) Le Bail, A. *Mater. Res. Bull.* **1988**, *23*, 447.

(9) Murray, A. D.; Fitch, A. N. *Mprofil Program for Le Bail Decomposition and Profile Refinement*, 1990.

(10) Atomare, A.; Burla, C.; Cascarano, C.; Giacovazzo, C.; Gualiardi, A.; Polidori, G.; Carnalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(11) Rietveld, H. M. *J. Appl. Crystallogr.* **1969**, *2*, 65.

(12) Larson, A.; Von Dreele, R. B. *GSAS Manual, Los Alamos Report* No. LA-UR-86-748, 1986.

S0897-4756(97)00173-7 CCC: $14.00

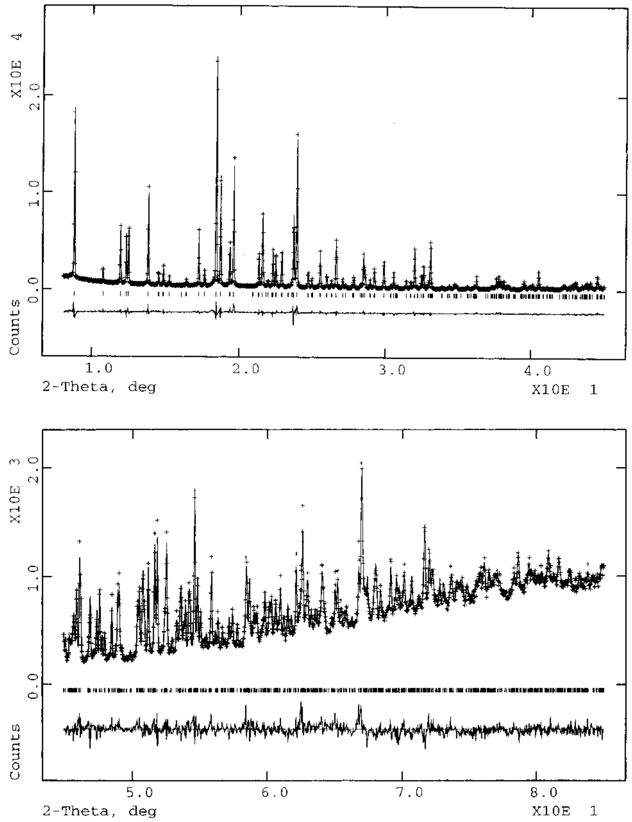

Figure 1. Experimental (+) and simulated (solid line) X-ray powder diffraction patterns for pure silica ITQ-4 (wavelength 1.399 96 Å) following Rietveld refinement. Vertical ticks indicate the positions of the allowed reflection for space group *I*2/*m*. Lowest trace is the difference plot.

Table 1. Crystallographic Data

data collection temperature	298 K
wavelength	1.399 96 Å
profile range	6−85°
step scan increment	0.01°
count time	2 s/p ($2\theta = 6-33.6°$) 6 s/p ($2\theta = 33.6-85°$)
space group	*I*2/*m* (12)
a	18.65243 (13)
b	13.49597 (8)
c	7.63109 (6)
β	101.9781 (5)°
no. of obsns	10199
no. of reflns	973
no. of independent reflns	248
no. of profile parameters	7
no. of structural parameters	46
R_{wp}	0.0767
R_p	0.0558
R_b	0.0644
χ^2	3.339

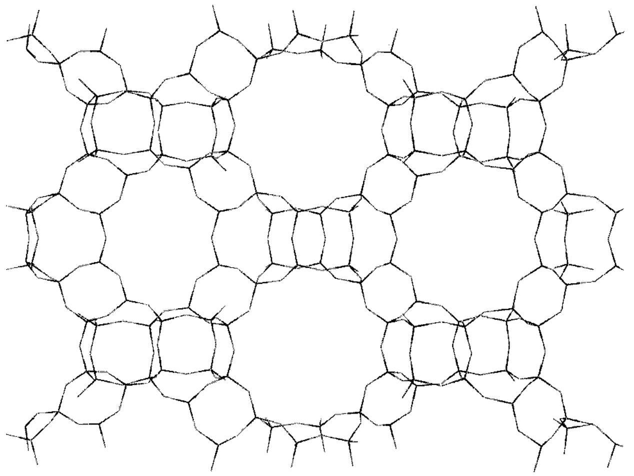

Figure 2. Framework topology of ITQ-4 in a perspective view along the normal to the *ab* plane. The lines at the lower left corner define the unit cell limits. (Figures 2−4 were produced with the software Weblab Viewer from Molecular Simulations, Inc. In all these figures Si is depicted as black and O as gray.)

Table 2. Fractional Atomic Coordinates and Isotropic Temperature Factors for the Asymmetric Unit of ITQ-4 (Space Group *I*2/*m*) with Standard Deviation in Parentheses[a]

atom	*x*	*y*	*z*	$U_i/U_e \times 100$
Si(1)	−0.01265(16)	0.11371(21)	0.2918(4)	2.02(10)
Si(2)	0.249813(17)	0.11336(19)	0.6215(5)	2.25(11)
Si(3)	0.14687(15)	0.11588(19)	0.2469(4)	1.75(11)
Si(4)	0.16169(16)	0.20243(21)	−0.1058(5)	2.33(10)
O(5)	0.31979(26)	0.17940(33)	0.6417(8)	1.65(7)
O(6)	−0.07340(31)	0.18435(30)	0.1910(8)	1.65(7)
O(7)	0.0	0.12865(57)	0.5	1.65(7)
O(8)	0.06025(31)	0.13926(28)	0.2230(7)	1.65(7)
O(9)	0.15762(31)	0.0	0.2024(10)	1.65(7)
O(10)	0.18823(30)	0.13830(30)	0.4442(9)	1.65(7)
O(11)	−0.03438(34)	0.0	0.2395(10)	1.65(7)
O(12)	0.21031(27)	0.13257(33)	0.7932(9)	1.65(7)
O(13)	0.27006(33)	0.0	0.6233(10)	1.65(7)
O(14)	0.17722(26)	0.17880(34)	0.0971(9)	1.65(7)

[a] The isotropic temperature factors of the O atoms were constrained to be equivalent during the refinement.

Table 3. Assignment of the ^{29}Si MAS NMR Peaks Based on the Average T−O−T Angles

chemical shift (ppm from TMS)	relative peak area	Si site	av T−O−T angle (deg)	
			^{29}Si NMR[13]	crystallographic
−107.97	1	Si(4)	142.5	143.9
−109.71	1	Si(2)	145.5	146.9
−110.86	1	Si(3)	147.5	147.4
−112.52	1	Si(1)	150.3	150.4

lengths vary between 1.548(7) and 1.666(4) Å (average 1.603 Å), with the O−Si−O bond angles having values between 106.30(4) and 113.68(32)° (average 109.46°). These values (for which no constraints were used) are well within the acceptable range reported for Rietveld refinements of zeolites. On the other hand, the average Si−O−Si bond angles for every Si site derived from our model agree remarkably well with those calculated from the ^{29}Si MAS NMR chemical shifts[2] using the equation of Thomas et al.[13] (Table 3). We conclude that the high crystallographic order of this defect-free pure silica phase allowed us to derive very precise structural information.

The framework structure of ITQ-4 is shown in Figure 2. It contains a one-dimensional large-pore sinusoidal channel running along the c crystallographic direction. This is a large-pore 12-membered ring (12MR) channel (zeolitic channels are usually classified according to the number of oxygens in the ring defining their minimum apertures). The smallest 12MR window in this channel (Figure 3, left) is highly puckered, with maximum and minimum distances between opposite oxygens of 7.2 and 6.2 Å, respectively (assuming the van der Waals radius of O to be 1.35 Å). However, the sinuosity of the channel effectively implies a modulation of the channel section and thus between two adjacent 12MR there is a void space of roughly 11.2 Å × 7.3 Å × 5 Å (Figure 3, right).

---

(13) Thomas, J. M.; Klinowski, J.; Ramdas, S.; Hunter, B. K.; Tennakoon, D. T. B. *Chem. Phys. Lett.* **1983**, *102*, 158.

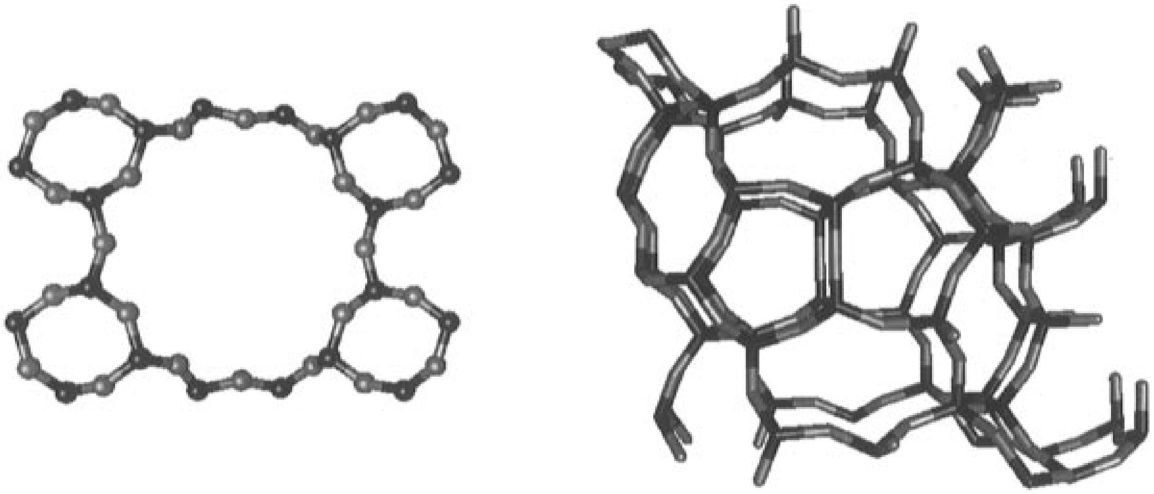

Figure 3. Ball-and-stick representation of the smallest 12MR window defining the minimum apertures of the channels in ITQ-4 (left), and stick model of the channel (right) showing the large void space limited by two adjacent 12MR windows.

The separation between each channel in ITQ-4 and the adjacent channels is a single chain of alternating 4MR and 6MR, i.e., the separation is a single T atom thick, as opposed to other silica polymorphs, for example SSZ-24, where the walls between channels are 2 T atoms thick.[14] As a consequence, there is a higher density of channels in ITQ-4. This feature, which is unique to ITQ-4, together with the modulation of the channels due to the sinuosity explains the surprisingly large void volume fraction of this 1D 12MR zeolite (0.21 cm^3/g, compared with 0.12 cm^3/g for SSZ-24,[15] the 1D 12MR zeolite with the largest pore opening). Among the known pure silica polymorphs, this void volume is succeeded only by that of pure silica zeolite Beta (0.22 cm^3/g),[4] a 3D large-pore material. We note that for catalytic purposes, for example in the isomerization of *n*-alkanes, 12MR 1D channel systems show good activity and selectivity.

The secondary building unit (SBU)[16] of ITQ-4 is the 4MR, since the complete framework can be built using only this structural entity. Such a unit was formerly supposed to be unfavorable for high silica materials, although this has been proved wrong by the subsequent synthesis of SSZ-24[15] and pure silica sodalite[17] (whose SBUs are also the 4MR). In ITQ-4 there is a small so-called "double crankshaft" chain containing five 4MR fused in a row parallel to (100). There are also 5MR and 6MR, from which a convenient tertiary building unit can be defined, as shown in Figure 4, from which the structure is easily constructed. This unit is made out of two [$4^3 5^2 6$] small cages sharing a 4MR.

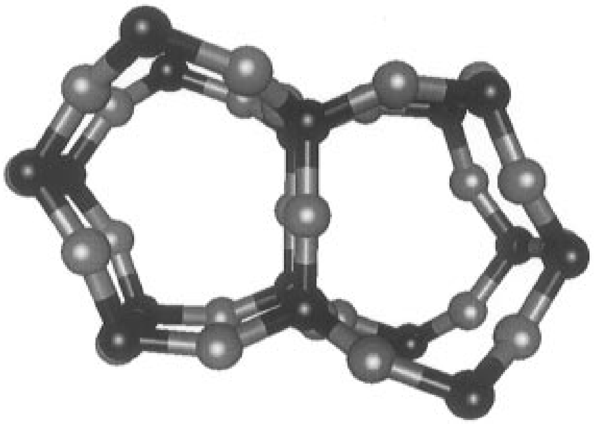

Figure 4. Ball-and-stick model of a tertiary building unit of ITQ-4, consisting of two [$4^3 5^2 6$] small cages sharing a 4MR, from which the whole ITQ-4 topology can be easily constructed.

In conclusion, ITQ-4 is a new microporous pure silica polymorph with a large 12MR sinusoidal channel. The sinuosity and the particularly high density of channels in the structure explain its void volume, which is exceptionally large for a one-dimensional channel system. The structural solution by direct methods from powder synchrotron diffraction data was greatly facilitated by the high degree of crystallographic order, which arises from the absence of Si−OH groups and Al atoms.

Acknowledgment. The authors gratefully acknowledge the Spanish DGICYT (MAT 94-0359-C02-01) for financial support.

Supporting Information Available: Listing of Si−O bond distances and O−Si−O angles (1 page). Ordering information is given on any current masthead page.

CM970173W

---

[14] Meier, W. M.; Olson, D. H.; Baerlocher, Ch. *Atlas of Zeolite Structure Types*; Elsevier: Amsterdam, 1996.

[15] Van Nordstrand, R. A.; Santilli, D. S.; Zones, S. I. *ACS Symp. Ser.* **1988**, *368*, 236.

[16] SBU is a concept of value for the classification of zeolitic structures, despite there being no evidence that these units bear any relation to the actual units from which the crystals grow.

[17] Bibby, D. M.; Dale, P. *Nature* **1985**, *317*, 157.