ITQ-7: A New Pure Silica Polymorph with a Three-Dimensional System of Large Pore Channels**

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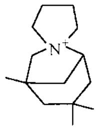
Zeolites find widespread uses in a number of technologically important areas, including adsorption, separation, and catalysis.[1] For some of these applications it is desirable that the zeolite possesses a three-dimensional system of large pores, since this greatly facilitates the diffusion of relatively large molecules into and out of the zeolite void space and in turn minimizes pore blockage. Additionally, it may also be important that the zeolite can be prepared with high Si/Al ratios, since this improves the chemical, thermal, and hydrothermal stability as well as the hydrophobicity, while at the same time modifying the reactivity and distribution of the active sites. However, despite considerable synthetic efforts throughout the last three decades, zeolite Beta is the only known zeolite to possess a three-dimensional system of large pores that can be directly synthesized with Si/Al ratios higher than around 5.[2] Zeolite Beta is a complex intergrown structure of at least two polymorphs, with all of them possessing large pores defined by windows that contain 12 TO$_{4/2}$ tetrahedra (12MR windows, where T = Si or Al).[3]

Our ongoing project on the synthesis of pure and high-silica zeolites in a fluoride-containing medium has produced a number of new pure silica materials during the last three years, including structures with a remarkably low framework density and a high void space.[4] We report here the synthesis and structure of ITQ-7 (*I*nstituto de *T*ecnología *Q*uímica number **7**), a new high-silica zeolite with a three-dimensional system of large pore 12MR channels. This material has a very low framework density ($FD = 15.37$, FD = number of Si per 1000 Å^3) which ranks it as the least dense phase ever reported amongst pure silica polymorphs along side chabazite ($FD = 15.40$). ITQ-7 is structurally related to zeolite Beta ($FD = 15.6$)[5] and its successful synthesis has a certain degree of a priori design.

The synthesis was performed with a new rigid and well-defined organic structure directing agent (SDA) in the presence of fluoride ions. The SDA spyro cation **I** (1,3,3-trimethyl-6-azoniumtricyclo[3.2.1.4^{6,6}]dodecane) is a modification of the SDA used to produce ITQ-3, ITQ-9, SSZ-31, and some materials that may be intergrowths of zeolite Beta and SSZ-31 (1,3,3,6,6-pentamethyl-6-azoniumbicyclo[3.2.1]octane, SDA **II**).[6] The modification consists of the quaternization of the nitrogen atom of the parent amine with $\mathrm{Br(CH_2)_4Br}$ rather than $\mathrm{CH_3I}$ in order to form a new ring that gives the whole SDA a larger volume while maintaining a rather rigid conformation. This change was aimed at altering the structure-directing effect to produce a zeolite with an enhanced void space or pore dimensionality as well as to make it more specific, since rigidity and volume are considered amongst the most important features that endow a particular SDA with structure-direction specificity.[7]



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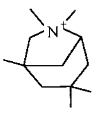

II

The strategy of using this large, rigid cation in a hydrothermal synthesis in an aqueous fluoride-containing medium afforded the pure silica ITQ-7. A new three-dimensional 4-connected framework of $\mathrm{SiO_4}$ tetrahedra was produced after calcination. ^{29}Si MAS NMR spectroscopic analysis (Figure 1)[8] shows calcined ITQ-7 contains essentially no Si-O-Si connectivity defects, since it is hard to detect any resonance around $\delta = -102$ in the spectrum that can be assigned to Si–OH species. Furthermore, the spectrum shows some resolution of Si(OSi)$_4$ sites, which are assigned to Si species in crystallographically distinct environments in the structure. Calcined ITQ-7 has a large micropore volume (around 0.22 cm^3 g^{-1}, determined by N_2 adsorption with the t-plot method) and large pores (6.8–6.9 Å, determined by Ar adsorption with the Horvath–Kawazoe method).

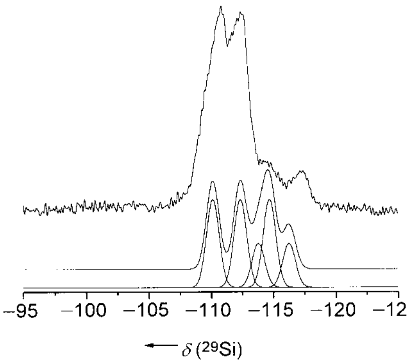

Figure 1. ^{29}Si MAS NMR spectra of calcined pure silica ITQ-7: experimental spectrum (top) and simulations using the equation of Thomas et al.[8] and the average Si-O-Si angles for each of the crystallographic sites found in this work (bottom).

The XRD pattern of calcined ITQ-7 can be indexed as tetragonal ($a = 12.88$ Å, $c = 25.27$ Å) and shows systematic absences consistent with space group $P4_2/mmc$ (and other subgroups). The pattern itself resembles that of the structure C described by Newsam et al. as a hypothetical framework related to polymorphs A and B of zeolite Beta.[3] Furthermore, the cell dimensions and symmetry of structure C (tetragonal, $a = 12.81$, $c = 13.00$ Å, space group $P4_2/mmc$) suggests a close structural relationship between both topologies. Structure C has a three-dimensional system of large 12MR channels that intersect perpendicularly. In contrast to polymorphs A and B, all the channels in structure C are linear.[3] We thus adopted a model building approach starting from structure C and looking for a transformation that could account for the doubling of the c edge in ITQ-7. It became clear that structure C can be easily constructed from the

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simple stacking of a given sheet normal to the *a* or *b* direction, without any translation or rotation. Since the connection between each layer is accomplished through double four member ring units (D4MR), when consecutive sheets are rotated 90°, full connectivity between the layers can still be accomplished and a new structure different from structure C (and the related polymorphs of the zeolite Beta) can be formed. The maximum topological symmetry of this new topology is maintained at $P4_2/mmc$ and a doubling of the *c* edge of the cell is required to describe the structure, which suggests that it could be ITQ-7.[9] The relationship between the topologies of ITQ-7 and structure C is illustrated in Figure 2. The model obtained for ITQ-7 was then optimized by a distance least squares procedure (program DLS76),[10] and the refined coordinates produced were used to simulate the powder XRD pattern, which was immediately recognized as that of ITQ-7. Finally, Rietveld refinement of this model in the topological symmetry ($P4_2/mmc$) against the XRD data of calcined ITQ-7 obtained with conventional $\mathrm{Cu_{K\alpha}}$ radiation was undertaken.

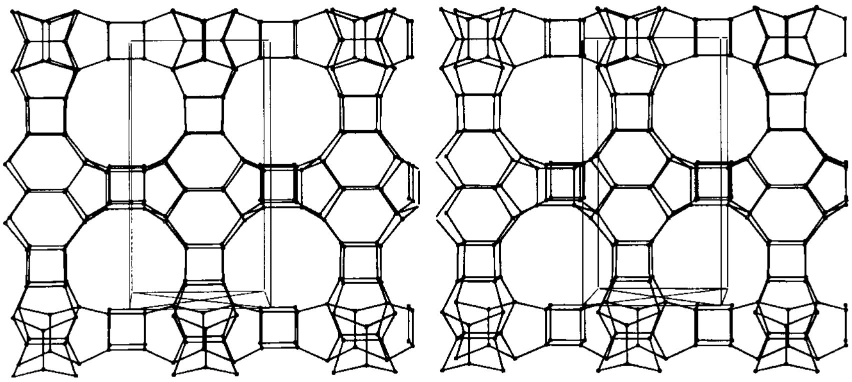

Figure 3. Stereo representation of the structure of ITQ-7 along [100]. Only connectivity between tetrahedral atoms is depicted.

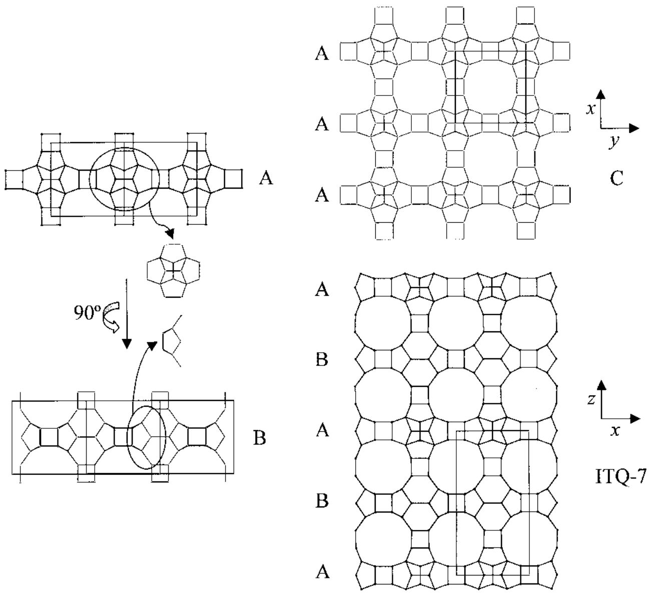

Figure 2. The relationship between the structures of ITQ-7 and the hypothetical structure C proposed by Newsam et al. for zeolite Beta.[3] A tertiary building unit common to ITQ-7, and the polymorphs A, B, and structure C proposed by Newsam et al.[3] (center of the left hand side) may be used to build a layer that is common to ITQ-7 and structure C. Connection of these layers without rotation through double four member rings yields structure C. The ITQ-7 topology is obtained when successive layers are rotated by 90° and connected in the same way.

ITQ-7 has a new zeolite topology (Figure 3) which is closely related to those of polymorphs A, B, and the hypothetical structure C proposed by Newsam et al. for zeolite Beta.[3] All these topologies may be built from the tertiary building unit shown in Figure 2. Different arrangements of this tertiary building block give rise to three-dimensional 4-connected nets containing a three-dimensional system of 12MR pores. All four topologies have linear pores along two directions, while the third pore is sinusoidal in polymorphs A and B but linear in structure C. The channel running along the *c* direction in ITQ-7 is sinusoidal but has large linear sections of around 21 Å. This may give rise to different catalytic behavior of the corresponding aluminosilicates, as the linear sections in the *c* direction will put different steric restrictions on transition states in ITQ-7 relative to zeolite Beta.

An interesting feature in ITQ-7 is the presence of double four member ring cages, a structural unit that was usually considered to be very unfavorable for high-silica zeolites. However, pure silica octadecasil synthesized in the presence of fluoride ions presents a D4MR with the fluoride ion located inside this cage. This material gives a characteristic ^{19}F MAS NMR resonance at $\delta = -38.2$ or -38.5, depending on the nature of the countercation.[11] The ^{19}F MAS NMR spectrum of noncalcined ITQ-7 suggests the F$^-$ ions are also located inside the D4MR, as evident from its chemical shift (Figure 4). Actually, there are two symmetrically different types of D4MR cages in ITQ-7 and the ^{19}F MAS NMR clearly consists of two overlapping resonances centered around $\delta = -38.5$ and -39.3, which strongly suggests that F$^-$ ions are located in both types of cages. Chemical analysis (F content: 1.69%) points to the full occupancy of the cages by F$^-$ ions.

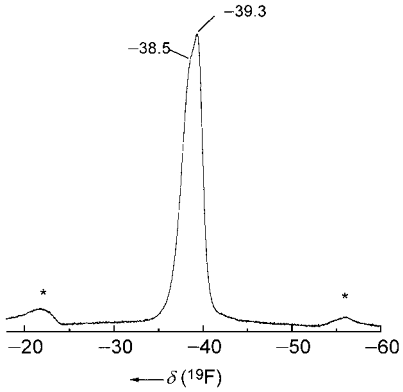

Figure 4. ^{19}F MAS NMR spectrum of noncalcined pure silica ITQ-7. Spinning side bands are marked with an asterisk.

However, the ^{29}Si MAS NMR spectrum shown in Figure 1 does not completely agree with that expected (five signals for

$Si(OSi)_4$ sites with relative intensities 2:2:2:1:1), which, in our view, may be a strong suggestion that the actual symmetry of ITQ-7 is lower than $P4_2/mmc$ (possibly $P4_222$ or $P4_2$). However, we don't find any evidence for this symmetry lowering in the low resolution XRD data, and attempts to refine the model in a lower symmetry were less satisfactory. High resolution XRD data with synchrotron radiation will be necessary to clarify this point.

Finally, preliminary energy minimization calculations of the SiO_2 framework using the GULP code[12] and the potential model of Sanders et al.[13] gave no evidence for a lower symmetry of ITQ-7, with the energy and cell dimensions being essentially equivalent in $P4_2/mmc$, $P4_222$, and $P1$ space groups. On the other hand, the calculations gave the following order of stability for SiO_2 frameworks: polymorph A > structure C > ITQ-7. We believe the successful synthesis of ITQ-7 is the result of combining two main structure-direction effects that allow us to overcome the energy penalty for this topology. The fluoride ion may show a preference towards structures containing very small cavities such as the D4MR,[6] and thus it may exert some structure-direction effect in favor of ITQ-7 rather than zeolite Beta.[14] On the other hand the shape, size, and rigidity of the SDA apparently favors ITQ-7 rather than structure C (which also contains D4MR units), possibly as a consequence of the bent shape of the cation and the different tortuosity of the channels in both topologies. We are currently investigating the structure-direction issues in the synthesis of ITQ-7, as crystallizations in different conditions may change the phase selectivity of the crystallization from ITQ-7 to zeolite Beta. Additionally, we have found evidence that, depending on the precise synthetic conditions, ITQ-7 samples may present intergrowths, the nature of which are currently under investigation.[18]

Experimental Section

Synthesis: Pure silica ITQ-7 was synthesized by using the hydroxide form of **I** as a structure directing agent. This was prepared by quaternization of the parent compound 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane (Aldrich) with 1,4-dibromobutane (99 %, Aldrich) in a NaOH solution under reflux. The organic product was extracted with CH_3Cl. Evaporation of this solvent gave a solid product (93 % yield), which was washed with diethyl ether and recrystallized from a mixture of methanol and ethyl acetate. The bromide salt was finally exchanged to the hydroxide form on an anion exchange resin. The zeolite was crystallized under hydrothermal conditions (PTFE-lined stainless-steel autoclaves, 150 °C, rotation (60 rpm), 15 days, pH 6.9, composition: SiO_2:$C_{14}H_{26}NOH$:HF:H_2O = 1:3:3:5.4) and contained the organic cation intact, as revealed by ^{13}C MAS NMR and chemical analysis. The analysis also shows the charge is neutralized by occluded F^- ions (elemental analysis: found: C 14.84, N 1.23, H 2.40, F 1.69; calculated for the ideal unit cell of composition $[C_{14}H_{26}NF]_4[SiO_2]_{64}$: C 14.14, N 1.18, H 2.20, F 1.60). After calcination of the sample at 580 °C both the SDA and the fluoride ions are removed from the material.

Structure analysis: An X-ray powder diffraction pattern of calcined pure silica ITQ-7 was collected at room temperature with a step size of 0.01° for scan times of 11 s and 44 s per step over the ranges $2^\circ \leq 2\theta \geq 40^\circ$ and $40^\circ \leq 2\theta \geq 85^\circ$, respectively, using conventional $Cu_{K\alpha}$ radiation (Philips X'Pert diffractometer in flat plate mode). Profile refinement of the structural model derived from model building (see above) was performed by the Rietveld method[15] with the GSAS program[16] without the use of geometrical constrains. The profile was matched in the range $12^\circ \leq 2\theta \leq 75^\circ$ because of the large asymmetry of the peaks at low 2θ angles and the very poor signal to noise ratio of the data at very high angle. A pseudo Voigt function, together with a manually interpolated background, was used to describe the peak shape.[17] A preferred orientation correction along the [001] direction and a peak broadening correction were applied. The final refinement used 62 variables and gave $R_{wp} = 10.76$, $R_p = 8.27$, $R_b = 6.26$, and $\chi^2 = 2.897$. The average Si–O bond length and Si-O-Si and O-Si-O angles are 1.59 Å, 109.3°, and 151.9°, respectively. The final atomic coordinates are given in Table 1 and Figure 5 shows the Rietveld plot. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666, e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-410723.

Table 1. Atomic coordinates of ITQ-7 ($[SiO_2]_{64}$, tetragonal, $P4_2/mmc$, a = 12.8528(4), c = 25.2136(8) Å).

Atom	*x*	*y*	*z*
Si(1)	0.1192(5)	0.1146(5)	0.06251(17)
Si(2)	0.3062(5)	0.2511(5)	0.90459(22)
Si(3)	0.5	0.1167(6)	0.06146(26)
Si(4)	0.3822(5)	0.3849(5)	0.18813(18)
Si(5)	0.3793(7)	0.3880(6)	0
O(6)	0.1426(12)	0.1313(12)	0
O(7)	0.1512(11)	0	0.0788(6)
O(8)	0	0.1379(10)	0.0742(6)
O(9)	0.2002(9)	0.1888(9)	0.0870(3)
O(10)	0.3996(6)	0.1685(9)	0.9116(3)
O(11)	0.3197(8)	0.3334(9)	0.9486(3)
O(12)	0.3205(8)	0.3027(9)	0.8453(4)
O(13)	0.5	0	0.0759(6)
O(14)	0.5	0.1373(15)	0
O(15)	0.5	0.3733(14)	0
O(16)	0.3327(18)	0.5	0
O(17)	0.3584(7)	0.3584(7)	0.25
O(18)	0.5	0.3626(12)	0.1782(6)
O(19)	0.3552(12)	0.5	0.1725(6)

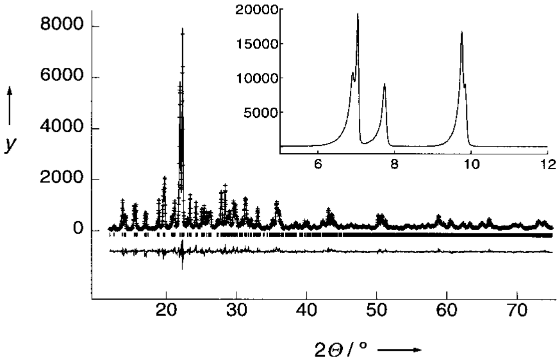

Figure 5. Observed (+) and calculated (solid line) X-ray diffraction patterns for calcined pure silica ITQ-7 ($Cu_{K\alpha}$ radiation) following Rietveld refinement. Vertical ticks indicate the positions of allowed reflections in the $P4_2/mmc$ space group. The lower trace is the difference plot. y = intensity (counts). The insert shows the low 2θ angle region, which was excluded from the refinement because of the extreme asymmetry of the peaks caused by axial divergence of the X-ray beam.

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[18] Note added in proof (May 25, 1999): The structure of ITQ-7 has been given the code ISV by the International Zeolite Association.

Interaction of a PDZ Protein Domain with a Synthetic Library of All Human Protein C Termini[**]

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Through increasingly efficient sequencing of genes and whole genomes, the amino acid sequences of unknown proteins are being deduced at an accelerating rate. This means that questions about the function of these identified proteins in the corresponding organisms are becoming increasingly important. Alongside the "classical" approaches to analyzing the roles of these proteins by molecular biological/biochemical methods, through the use of bioinformatics it is possible to gain information about the new protein by sequence comparisons with proteins of known function. At the same time it has been demonstrated that large globular proteins are usually built up of individual domains that show independent folding and functions. Many of these domains are protein modules which occur in a number of, often unrelated, proteins.[1] Protein sequence comparison not only reveals known protein domains, but also may identify novel, previously undetected stretches of homologous sequence in the new proteins.[2] While known domains potentially point to the role of a protein, the function of new domains must be derived experimentally. Generally, protein domains can be produced by recombinant technology and folding in vitro. Many of them play a role in signal transduction and regulation processes where the identification of binding partners is a basic step towards discovering their function. To accomplish this, usually biologically generated protein libraries are enlisted to screen for the potential binding partner of the newly discovered domain.[3]

We report here the chemical synthesis of a new kind of library, designed to discover binding partners for a PDZ

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