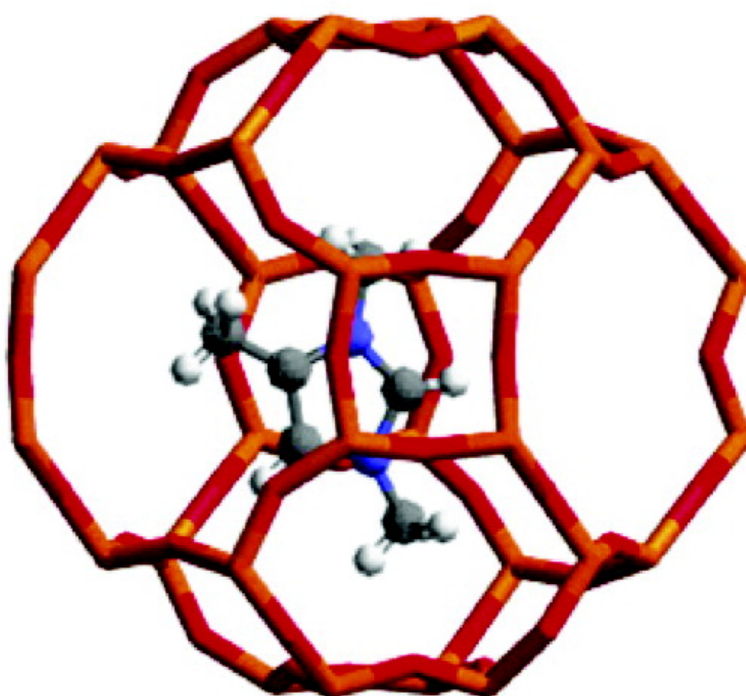


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## Synthesis and Crystal Structure of As-Synthesized and Calcined Pure Silica Zeolite ITQ-12

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**Abstract:** The small-pore pure silica zeolite ITQ-12 has been synthesized with fumed silica as the silica source in the presence of 1,3,4-trimethylimidazolium hydroxide and hydrofluoric acid under hydrothermal conditions at 448 K. Rietveld refinement using synchrotron X-ray diffraction data of the calcined ITQ-12 product taken at 298 K confirms the proposed topology, framework type code **ITW**, which can be described by a monoclinic unit cell  $[\text{Si}_{24}\text{O}_{48}]$  having *Cm* symmetry. Unit cell parameters are  $a = 10.3360(4)$ ,  $b = 15.0177(6)$ , and  $c = 8.8639(4)$  Å,  $\beta = 105.356(3)^\circ$ , and cell volume  $V = 1326.76(9)$  Å<sup>3</sup>. For as-synthesized ITQ-12, the occluded fluoride anion is located inside the double four-membered ring, while the flat 1,3,4-trimethylimidazolium cation lies on the equatorial plane of the slit-shaped  $[4^45^46^48^4]$  cage, with its longest dimension in the  $[010]$  direction. The monoclinic unit cell  $[(\text{C}_6\text{N}_2\text{H}_{11})^+\text{F}_2^-][\text{Si}_{24}\text{O}_{48}]$ , having *Cm* symmetry, has parameters  $a = 10.4478(3)$ ,  $b = 14.9854(4)$ , and  $c = 8.8366(3)$  Å,  $\beta = 105.935(2)^\circ$ , and cell volume  $V = 1330.34(7)$  Å<sup>3</sup> at 298 K. Cooperative structure-directing effects during the crystallization of ITQ-12 are discussed in terms of the structure of the as-made material.

### Introduction

There are over 140 different zeolite framework structures, most having multiple isotopes of different designations and compositions,<sup>1</sup> but there are few pure silica, small-pore (8-ring) zeolites. However, the number of synthetic small-pore pure silica zeolites has been increasing in recent years due to developments of new synthetic routes, such as employing a wide variety of new structure-directing agents (SDAs) and use of fluoride anion, etc.<sup>2–5</sup> Recently the use of 8-ring, pure or high silica zeolites and  $\text{AlPO}_4$ 's as adsorbents for the pressure swing adsorption (PSA) separation of propene from propene/propane mixtures has been proposed, making use of the molecular sieving properties of these materials.<sup>6–8</sup> This may stimulate research

aimed at the synthesis of additional small-pore zeolites and reveal new structures as well as more cost-effective synthetic pathways.

$[\text{Si}_{24}\text{O}_{48}]$ -**ITW**-ITQ-12 is an 8-ring pure silica zeolite recently reported by Boix et al.<sup>9</sup> Its structure contains obloid  $[4^45^46^48^4]$  cages having  $\sim 3.9$  Å  $\times$   $9.6$  Å  $\times$   $8.5$  Å internal size. The cages are linked together by double 4-rings (D4R), forming a 3-D topology. There are two types of 8-ring cage openings. One of them ( $2.4$  Å  $\times$   $5.3$  Å) appears too narrow to allow passages of even the smallest hydrocarbon. The other type of 8-ring possesses a  $3.8$  Å  $\times$   $4.1$  Å opening, which is close to the cross sections of propene and propane molecules.<sup>10</sup> As far as we know, this topology has never been proposed as a hypothetical zeolite topology. A significant molecular sieving effect has been observed for propene and propane adsorption in ITQ-12.<sup>10,11</sup> At 303 K, the ratio of diffusion coefficients for propene and propane in ITQ-12 is greater than  $\sim 100$ . Furthermore, at 353 K, essentially no propane adsorption is observed.<sup>11</sup> This superb property makes ITQ-12 a very promising adsorbent for a new,

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more efficient PSA process for the separation of propene/propane from their mixtures. Propene/propane separation is an important and large-volume operation in the chemical and petrochemical industry, and it is currently achieved using a very energy-intensive fractional distillation process.<sup>12–15</sup> The PSA separation of propene/propane using ITQ-12 has great potential to become a novel, more energy-efficient and cost-effective industrial process.

In the original procedure for the preparation of ITQ-12 described by Boix et al.,<sup>9,10</sup> tetraethyl orthosilicate (TEOS) is used as the silica source, which is transformed into silica gel through hydrolysis before crystallization. This procedure is unlikely to be realized in a manufacturing process of ITQ-12 because of cost factors and the emission of a large quantity of ethanol. A readily available and easily handled silica source is therefore needed to replace TEOS. Furthermore, because the framework structure of calcined ITQ-12 reported by Barrett et al. in a preliminary communication<sup>10</sup> was based on laboratory Cu K $\alpha$  X-ray powder diffraction data, a refinement based on higher resolution data is desirable. For as-synthesized ITQ-12 with occluded 1,3,4-trimethylimidazolium cation and fluoride anion as the SDAs, the locations of the SDA ions are of interest in order to gain a better understanding of the crystallization process and the SDA–zeolite structure relationships. The aims of the present work are (1) to demonstrate that fumed silica can be used as an alternative silica source for the synthesis of high-quality ITQ-12 to replace TEOS; (2) to obtain a more accurate structural model for the framework of ITQ-12 based on high-resolution synchrotron X-ray diffraction data; and (3) to locate the positions of the 1,3,4-trimethylimidazolium cation and fluoride anion in the as-synthesized ITQ-12.

## Experimental Section

**Synthesis of ITQ-12.** 1,3,4-Trimethylimidazolium iodide (TMII) was synthesized as follows. First, 34.5 g of 4-methylimidazole (Aldrich, 98%) was dissolved in 600 mL of chloroform (Fluka, p.a.). This solution was mixed with 128 g of potassium carbonate hydrate (Fischer, p.a.). A large excess (468 g) of iodomethane (Aldrich, 99%) was then added in two equal portions with a time interval of 3 days. After the mixture was stirred at room temperature for 6 days, the potassium carbonate was filtered out, and the solvent was removed by evaporation. The solid product (TMII, ca. 100 g) was washed using diethyl ether. The collected product, in D<sub>2</sub>O solution, shows <sup>1</sup>H NMR peaks at  $\delta$  = 8.54 (s, 1H), 7.17 (s, 1H), 3.84 (s, 3H), 3.77 (s, 3H), and 2.30 (s, 3H) ppm. The iodide salt was converted to the hydroxide form (1,3,4-trimethylimidazolium hydroxide, TMIOH) by (1) dissolution in a proper amount of water (50 g of solid:500 g of H<sub>2</sub>O) and (2) contacting with Dow X1 anion-exchange resin at room temperature for 14 h. The hydroxide solution was then concentrated under evacuation at 323 K to a total volume below 100 mL. The concentration of the solution was determined by HCl titration to be 1.16 M. Both the diluted and the concentrated hydroxide solutions exhibit <sup>1</sup>H NMR resonances at  $\delta$  = 8.54 (s, 1H), 7.17 (s, 1H), 3.83 (s, 3H), 3.77 (s, 3H), and 2.31 (s, 3H) ppm. However, the 8.5 ppm peak in the spectrum of TMIOH decreases in intensity rapidly (in minutes), due to a fast H–D exchange between the proton on C2 and D<sub>2</sub>O under these basic conditions.<sup>16</sup> For TMII, the intensity of the 8.5 ppm peak decreases more slowly, with

~10% remaining after 7 days. <sup>1</sup>H NMR verified the high purity of the iodide and the derived hydroxide products.

Two kinds of fumed silica, Degussa Aerosil 380 and Sigma fumed silica, were used as the silica sources in two preparations, respectively. For each, 2.7 g of fumed silica was blended into 21 g of the concentrated 1,3,4-trimethylimidazolium hydroxide (TMIOH) solution and stirred vigorously for 2 h. A tiny amount of uncalcined ITQ-12 (less than 1 mg) was added into the slurry as seeds for crystallization. To the gel was added 1.1 g of 49 wt % HF solution, and the mixture was further stirred for 1 h. The gel was weighed to determine the amount of water (water content of the fumed silica was neglected). The calculated gel composition was 1 SiO<sub>2</sub>:0.56 TMIOH:0.62 HF:15 H<sub>2</sub>O. This gel was sealed in a Teflon-lined stainless steel autoclave, heated to 448 K, and allowed to crystallize under static conditions for 10 days. The solid products were recovered, washed with ample amounts of water, and dried. Calcination was performed in a muffle furnace in static air at 1013 K for 6 h.

**Powder XRD.** Phase identity and purity of the synthetic products were first checked with X-ray diffraction on a Rigaku Geigerflex X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å). The diffractometer was equipped with a graphite secondary monochromator and a scintillation counter.

The synchrotron X-ray powder diffraction data for both calcined and as-synthesized samples were collected at 298 K at the X7A beamline of the National Synchrotron Light Source at Brookhaven National Laboratory. Monochromatic synchrotron X-ray ( $\lambda$  = 0.7103–(1) Å) was used in conjunction with a gas-proportional position-sensitive detector. Each sample, contained in a 0.3 mm glass capillary, was spun for better powder averaging, and the PSD was stepped in 0.25° intervals between 3 and 50° to produce 0.01° step scan data.

**Rietveld Refinement.** Rietveld refinement was performed with the GSAS program<sup>17</sup> using Brian Toby's EXPGUI Windows interface. A total of 3593 data points, 707 reflections, in the 2 $\theta$  range from 4.25° to 40°, were included for the refinement of the calcined ITQ-12 sample; data in the same 2 $\theta$  range were used for the as-synthesized sample. Backgrounds were fitted with shifted Chebyshev functions with 17 coefficients. For the fitting of peak profiles, pseudo-Voigt functions with one axial divergence asymmetry parameter were used. The unit cell model in the *Cm* symmetry according to ref 10 was applied as the starting model to refine the structure of the calcined sample. The Structure Commission of the International Zeolite Association has recently assigned the framework type code **ITW** to ITQ-12 type materials,<sup>18</sup> with maximum topological symmetry *C2/m*. The choice of space group *Cm* in this work will be discussed below.

**Calcined ITQ-12.** The model for calcined ITQ-12 was refined using soft constraints of 1.61 Å for Si–O bond lengths with weight values  $\sigma$  = 0.001 and overall weight FACTR = 1. Also, to reduce the number of variables and to avoid unnecessary divergences and inaccuracies, the isotropic temperature displacement factors for each individual atom type were constrained to be equal. The refinement was done with 84 variables. The resulting structure was then used for the refinement of the as-synthesized ITQ-12 structure.

**As-Synthesized ITQ-12.** The fluoride and 1,3,4-trimethylimidazolium (TMI) ions have to be introduced in proper positions in the voids of the above ITQ-12 framework model. From previous studies of the roles of the F<sup>–</sup> anion for crystallization of zeolitic frameworks, it is expected that the fluoride anion acts as a mineralizing agent or catalyst for the breaking and formation of Si–O–Si bonds and as a structure-directing agent for the formation of D4R cavities.<sup>19,20</sup> This is suggested by the presence in the structure of D4R cavities that have never been encountered in pure SiO<sub>2</sub> materials synthesized without the use of

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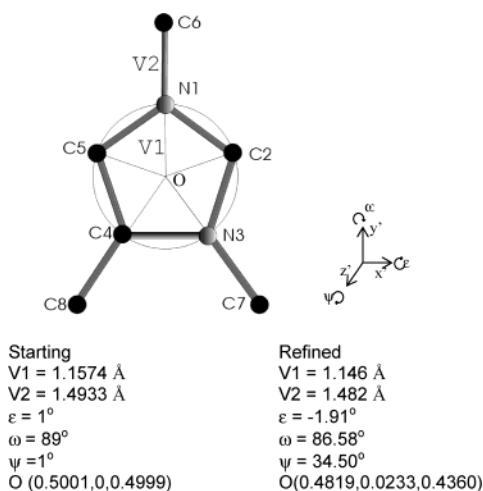
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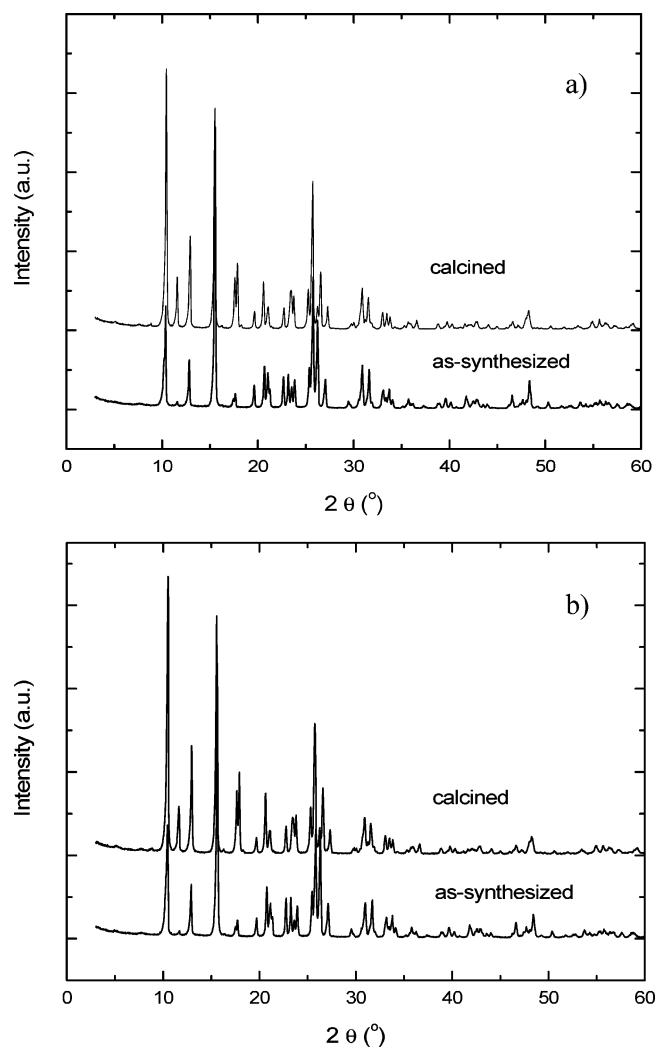
**Figure 1.** Rigid body parameters for the 1,3,4-trimethylimidazolium cation model.

fluoride. A single resonance at  $-40$  ppm in the  $^{19}\text{F}$  MAS NMR spectrum of the as-made ITQ-12 material is a clear indicator of the siting of the fluoride anions, located exclusively inside these small cavities in the structure.<sup>10,21</sup> Furthermore, chemical analysis points to a nearly complete occupancy by fluoride in these D4R cavities (1.97 F per unit cell, compared to 2 D4R per unit cell).<sup>10</sup> Thus, in the trial model, a F ion is set inside the D4R, i.e., at (0.5, 0.5, 0.5) with a full occupancy. Positions of all other atoms are allowed to refine together with unit cell parameters and other variables.

The SDA,<sup>22</sup> 1,3,4-trimethylimidazolium cation, must occupy the 32 T-atom [ $4^5 6^4 8^4$ ] cage. The planar shape of this organic cation can be modeled by using a rigid body with two different translation lengths. One translation length, V1, is to describe the aromatic 5-ring; the second translation length, V2, describes the three substituting methyl groups. H atoms are excluded because of their weak X-ray scattering powers. At our experimental temperature, 298 K, they are unlikely to contribute significantly to the diffraction intensities. Figure 1 shows the rigid body. Approximations are made in the rigid body settings: (1) the aromatic ring is taken as an ideal pentagon and (2) the substituting methyl carbon atoms are positioned with equal distances to their respective bonding ring atoms. Considering the symmetrical shape of the ITQ-12 cage and the possible orientations of TMI cations at the diffraction experiment conditions (298 K), these approximations seem justified. The initial values of the magnitudes of both translation lengths are taken from ref 23 by averaging the C–C and C–N bond lengths in and attached to an aromatic ring, respectively. The two translation lengths of the rigid body are refined independently. The starting origin of the rigid body was near the center of the large cage, i.e., at (0.5001, 0.0001, 0.4999). Its position was refined together with three additional rotation variables,  $\epsilon$ ,  $\omega$ , and  $\psi$ , of the Cartesian axes, starting with  $1^\circ$ ,  $89^\circ$ , and  $1^\circ$ , respectively.

**Molecular Simulation.** The Cerius<sup>2</sup> program of Accelrys was used to simulate the location of the 1,3,4-trimethylimidazolium (1,3,4-TMI) cation in ITQ-12. For comparison, another feasible SDA for ITQ-12 preparation, the 1,2,3-trimethylimidazolium (1,2,3-TMI) cation,<sup>10</sup> was

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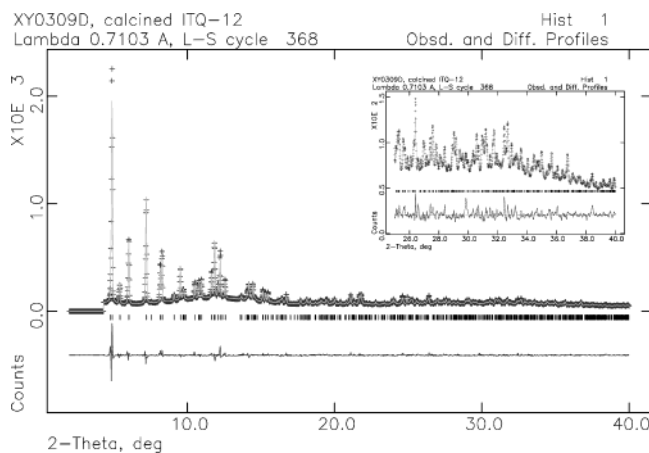
**Figure 2.** Powder XRD patterns of as-synthesized and calcined ITQ-12 made with (a) Degussa Aerosil 380 and (b) Sigma fumed silica.  $\lambda = 1.5418$  Å.

studied. Simulations were performed using an 18 Å interaction cutoff within a crystal section of  $4 \times 3 \times 5$  unit cells at 303 K and 101.3 kPa. Positions of the cations ( $5 \times 10^6$  configurations for each) were generated using the Monte Carlo method. The positions are accepted when they are energetically favorable: the pccf\_300\_1.01 force field was used.

## Results and Discussion

**Synthesis.** Off-white solid products were recovered from the mother liquors after 10 days of hydrothermal treatment at 448 K, starting with both Degussa Aerosil 380 and Sigma fumed silica. In comparison with the original synthetic procedure,<sup>9,10</sup> a significant improvement of the current work is the use of fumed silica instead of tetraethyl orthosilicate as the silica source. After calcination the solids become white. XRD patterns, obtained using the Cu K $\alpha$  radiation, of as-synthesized and calcined samples are depicted in Figure 2. The peak positions in these patterns are exactly the same as in the patent literature,<sup>9</sup> confirming that they are indeed ITQ-12. The product made with Sigma fumed silica was chosen for further synchrotron X-ray diffraction experiments.

**Structure Refinements.** Rietveld refinement of the calcined material, starting with the model proposed in ref 10, in the space



**Figure 3.** Observed (+) and calculated (solid line) powder X-ray diffractograms for calcined ITQ-12 refined in the space group  $Cm$ . Vertical tick marks indicate the positions of allowed reflections. The lower trace is the difference plot.  $\lambda = 0.7103(1)$  Å.

**Table 1.** Crystallographic and Experimental Parameters for Rietveld Refinement for Calcined ITQ-12

wavelength	0.7103(1) Å
temperature	298 K
$2\theta$ range	0–55° (used 4.25–40°)
step size	0.01°
no. of data points	3569
no. of reflections	707
space group	$C1m1$ (No. 8)
unit cell parameters (Å)	
<i>a</i>	10.3360(4)
<i>b</i>	15.0177(6)
<i>c</i>	8.86390(35)
$\beta$	105.3560(29)
cell volume (Å <sup>3</sup> )	1324.76(9)
residuals	
$R_{wp}$	0.0560
$R_p$	0.0425
$R_F^2$	0.0910
reduced $\chi^2$	40.95

group  $Cm$  with 20 unique atoms, rapidly converged, providing good agreement of the simulated and observed powder X-ray patterns (Figure 3). Table 1 lists the crystallographic and experimental parameters for the Rietveld analysis. The resulting atomic positions and isotropic temperature displacement factors are given in Table 2, and the refined structure is graphically shown in Figure 4.

This Rietveld refinement result confirms the correctness of the ITQ-12 framework topology proposed in ref 10. At 298 K, the structure is described with a monoclinic unit cell with  $Cm$  symmetry, having the unit cell formula [Si<sub>24</sub>O<sub>48</sub>]. The refined unit cell parameters are  $a = 10.3360(4)$ ,  $b = 15.0177(6)$ , and  $c = 8.8639(4)$  Å,  $\beta = 105.356(3)^\circ$ , and cell volume  $V = 1326.76(9)$  Å<sup>3</sup>. These numbers are close to those in ref 10. All refined Si–O bond lengths, with soft constraints applied, are in the narrow range from 1.593 to 1.625 Å, and the bond angles are realistic, with ranges O–Si–O from 99 to 120° and Si–O–Si from 131 to 163° (see Supporting Information). A satisfactory fit of the calculated and observed diffractograms was achieved ( $R_{wp}$ ,  $R_p$ , and  $R_F^2$  are 0.0560, 0.0425, and 0.0910, respectively). Thus, by virtue of the better quality of the synchrotron data, one unrealistically short Si–O distance and one sharp O–Si–O angle found in the previous work<sup>10</sup> now have more proper values.

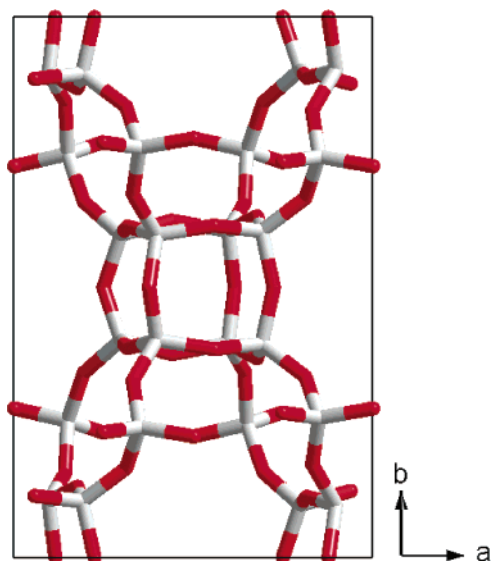
**Table 2.** Atomic Positions and Isotropic Temperature Factors for Calcined ITQ-12<sup>a</sup>

name	X	Y	Z	$U_{iso} \times 100$	occupancy
Si1	0.6520(20)	0.2467(8)	0.1090(18)	0.47(10)	1
Si2	0.6927(14)	0.3958(7)	0.6730(14)	0.47(10)	1
Si3	0.5995(13)	0.3955(6)	0.3176(14)	0.47(10)	1
Si4	−0.6469(21)	0.2417(9)	−0.1071(18)	0.47(10)	1
Si5	−0.6992(14)	0.4025(8)	−0.6643(14)	0.47(10)	1
Si6	−0.5997(12)	0.4026(8)	−0.2990(14)	0.47(10)	1
O7	0.6458(28)	0.3435(11)	0.1822(22)	0.71(15)	1
O8	0.4416(14)	0.3766(20)	0.2977(32)	0.71(15)	1
O9	0.6802(35)	0.3688(18)	0.4936(11)	0.71(15)	1
O10	0.7502(33)	0.2683(14)	−0.0002(42)	0.71(15)	1
O11	0.7270(43)	0.5	0.6915(40)	0.71(15)	1
O12	0.5034(29)	0.2241(9)	0.0012(61)	0.71(15)	1
O13	0.8148(24)	0.3347(15)	0.7629(26)	0.71(15)	1
O14	−0.6179(46)	0.5	0.2923(38)	0.71(15)	1
O15	−0.8025(26)	0.3418(14)	−0.7889(26)	0.71(15)	1
O16	−0.6207(44)	0.5	−0.2379(33)	0.71(15)	1
O17	−0.6665(25)	0.3272(12)	−0.2175(25)	0.71(15)	1
O18	−0.4403(14)	0.3857(21)	−0.2644(33)	0.71(15)	1
O19	−0.6810(32)	0.3875(19)	−0.4791(12)	0.71(15)	1
O20	−0.7478(39)	0.5	−0.7292(35)	0.71(15)	1

<sup>a</sup> Soft constraints applied to Si–O distances at 1.610 Å with  $\sigma = 0.001$ , overall weight FACTR = 1.

An inspection of the atomic positional values in Table 2 raises the suspicion that the true unit cell symmetry may be higher, having  $C2/m$  symmetry rather than  $Cm$ . However, there are a number of facts which militate against  $C2/m$  symmetry. First, as reported before,<sup>10</sup> <sup>29</sup>Si MAS NMR of calcined ITQ-12 indicates that there are five distinct Si environments with 1:1:1:1:2 populations in the −108 to −118 ppm region of chemical shifts, corresponding to Si(OSi)<sub>4</sub> species in at least five different crystallographic sites. This is inconsistent with  $C2/m$  predicting only three unique Si sites and thus is definite evidence that the symmetry must be lower than  $C2/m$ . These NMR results are fully consistent with the  $Cm$  model, as it has six Si sites with equal multiplicities. Furthermore, the earlier structure solution and refinement of the  $C2/m$  unit cell based on Cu K $\alpha$  X-ray diffraction data found a Si–O–Si bond angle of 180°, which is unrealistic. This linear Si–O–Si angle is caused by the siting of the O10 atom on an inversion center. We have now again refined the structure with the  $C2/m$  unit cell model using high-resolution synchrotron X-ray diffraction data. Details of the refinement and results are provided as Supporting Information. The  $R$  values for the refinement in the  $C2/m$  unit cell, which has the same diffraction conditions as  $Cm$ , are  $R_{wp} = 0.0581$ ,  $R_p = 0.0445$ ,  $R_F^2 = 0.1047$ , and reduced  $\chi^2 = 43.65$ , slightly higher than those for  $Cm$ . The unrealistically straight Si1–O10–Si1 is clearly seen in the refined model. This indicates again that  $C2/m$  is not a proper space group to describe the ITQ-12 framework. Finally, energy minimization calculations showed the structure in  $Cm$  to be more favorable than that in  $C2/m$  or  $C2$ .<sup>10</sup>

For the as-synthesized material with the occluded F<sup>−</sup> and TMI<sup>+</sup> ions, trial refinements were made for the occupancies of the F atom, and the C and N atoms in the rigid body. The occupancy of F refined to ca. 0.98, and the occupancies of C and N atoms in the  $Cm$  cell ranged between 0.4 and 0.7. Thus, in final refinement cycles, the occupancy factors were fixed at 1.0 for F and 0.5 for TMI atoms, respectively, to account for the chemical composition of ITQ-12 (nearly 2 F and 2 TMI per unit cell<sup>10</sup>). Using the experimental data and conditions listed in Table 3, a satisfactory fitting of the simulated XRD pattern



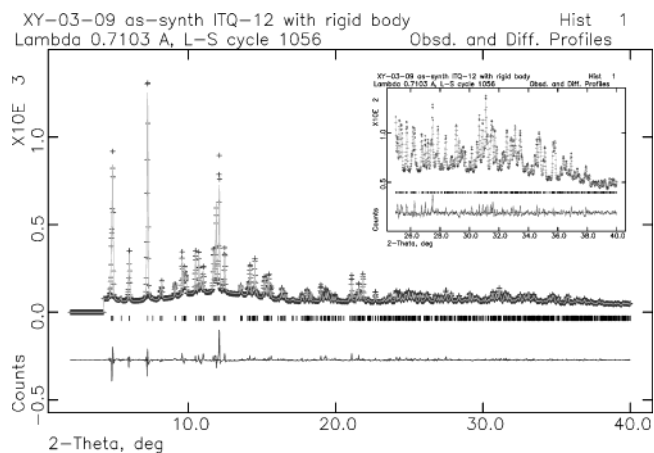
**Figure 4.** Refined unit cell structure of calcined ITQ-12 viewing down the  $z$  axis.

**Table 3.** Crystallographic and Experimental Parameters for Rietveld Refinement for As-Synthesized ITQ-12

wavelength	0.7103(1) Å
temperature	298 K
$2\theta$ range	0–55° (used 4.25–40°)
step size	0.01°
no. of data points	3574
no. of reflections	691
space group	$Cm1m$ (No. 8)
unit cell parameters (Å)	
$a$	10.4478(3)
$b$	14.9854(4)
$c$	8.8366(3)
$\beta$	105.935(2)
cell volume (Å <sup>3</sup> )	1330.34(7)
residuals	
$R_{wp}$	0.0550
$R_p$	0.0405
$R_F^2$	0.0749
reduced $\chi^2$	34.58

to the observed one can be achieved, as shown in Figure 5. The refined atomic positions are given in Table 4. The structure is illustrated in Figures 6 and 7.

A significant feature of the structure of as-synthesized ITQ-12, in comparison to the calcined one, is the differences in the unit cell parameters:  $a$  is larger and  $b$  and  $c$  are smaller, while the cell volume is only slightly larger (Tables 1 and 3). The unit cell has a chemical formula  $[(C_6N_2H_{11})_2F_2][Si_{24}O_{48}]$  (H atoms not included in the refined model). At 298 K, the values of refined cell parameters in the  $Cm$  cell are  $a = 10.4478(3)$ ,  $b = 14.9854(4)$ , and  $c = 8.8366(3)$  Å,  $\beta = 105.935(2)^\circ$ , and cell volume  $V = 1330.34(7)$  Å<sup>3</sup>. In the refined structure, the position of the fluoride anion is close to the center of the D4R cavity, as expected (Figure 6), and the Si–F distances are consequently in the expected range (average 2.645 Å). However, because of the slight D4R distortion, the Si–F distances within the D4R unit show a larger variation (2.54–2.76 Å) than those found in the other, more symmetric, pure silica material for which data are available: in the tetragonal as-made octadecasil (AST) with only two different Si–Si distances within the cube (3.036 Å ( $\times 8$ ) and 3.039 Å ( $\times 4$ ), compared to eight different distances ranging from 2.961 to 3.080 Å in ITW), all the Si–F



**Figure 5.** Observed (+) and calculated (solid line) powder X-ray diffractograms for as-synthesized ITQ-12 refined in the space group  $Cm$ . Vertical tick marks indicate the positions of allowed reflections. The lower trace is the difference plot.  $\lambda = 0.7103(1)$  Å.

**Table 4.** Atomic Positions and Isotropic Temperature Factors for As-Synthesized ITQ-12<sup>a</sup>

name	$x$	$y$	$z$	$U_{iso} \times 100$	occupancy
Si1	0.649(6)	0.2435(9)	0.120(6)	1.00(8)	1
Si2	0.697(5)	0.4012(9)	0.693(5)	1.00(8)	1
Si3	0.598(5)	0.3984(9)	0.331(5)	1.00(8)	1
Si4	−0.647(6)	0.2451(9)	−0.092(6)	1.00(8)	1
Si5	−0.690(5)	0.3981(8)	−0.649(5)	1.00(8)	1
Si6	−0.591(5)	0.3989(9)	−0.290(5)	1.00(8)	1
O7	0.659(6)	0.3296(12)	0.229(6)	1.49(14)	1
O8	0.442(5)	0.3736(25)	0.297(7)	1.49(14)	1
O9	0.689(6)	0.3869(16)	0.509(5)	1.49(14)	1
O10	0.747(6)	0.2406(20)	0.007(7)	1.49(14)	1
O11	0.753(6)	0.5	0.738(7)	1.49(14)	1
O12	0.505(6)	0.2238(9)	0.003(6)	1.49(14)	1
O13	0.817(6)	0.3448(11)	0.806(6)	1.49(14)	1
O14	0.615(8)	0.5	0.282(8)	1.49(14)	1
O15	−0.800(6)	0.3288(12)	−0.743(6)	1.49(14)	1
O16	−0.619(8)	0.5	−0.247(8)	1.49(14)	1
O17	−0.646(6)	0.3424(11)	−0.167(6)	1.49(14)	1
O18	−0.435(5)	0.3734(25)	−0.252(7)	1.49(14)	1
O19	−0.670(6)	0.3681(14)	−0.467(5)	1.49(14)	1
O20	−0.729(6)	0.5	−0.697(7)	1.49(14)	1
F1	0.5	0.5	0.5	0.45(11)	1
N1	0.504(7)	0.0848(16)	0.516(6)	0.98(10)	0.5
C2	0.518(7)	−0.0008(17)	0.564(6)	1.47(10)	0.5
N3	0.482(6)	−0.0531(16)	0.435(6)	0.98(10)	0.5
C4	0.446(6)	0.0002(17)	0.308(6)	1.47(10)	0.5
C5	0.460(6)	0.0855(16)	0.358(6)	1.47(10)	0.5
C6	0.533(8)	0.1645(18)	0.619(7)	1.47(10)	0.5
C7	0.482(7)	−0.1520(16)	0.434(6)	1.46(10)	0.5
C8	0.399(7)	−0.0297(23)	0.142(6)	1.47(10)	0.5

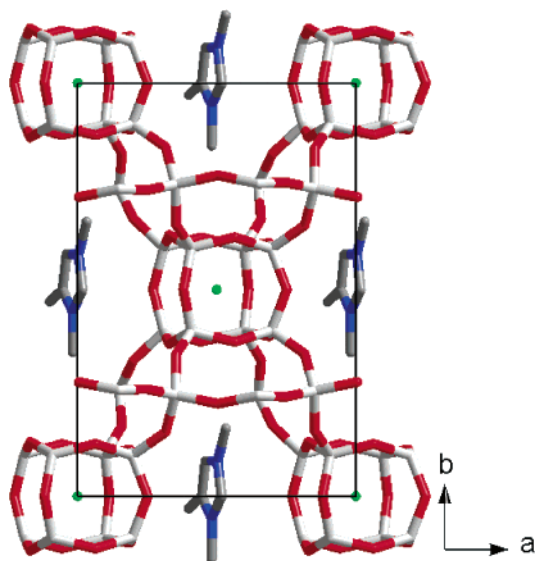
<sup>a</sup> Soft constraints applied to Si–O distances at 1.610 Å with  $\sigma = 0.001$ , overall weight FACTR = 1.

bonds are equal (2.623 Å)<sup>24</sup> (2.63 Å determined by NMR measurements<sup>25</sup>).

More interesting is the location of the TMI cation, which is consistent with the cage shape. The refined rigid body origin is at (0.4819, 0.02331, 0.4360), close to the center of ITQ-12 cage near ( $1/2, 0, 1/2$ ). The rotation vectors are  $\epsilon = -1.91^\circ$ ,  $\omega = 86.58^\circ$ , and  $\psi = 34.50^\circ$ . As shown in Figure 7, the planar molecule lies exactly on the equatorial plane of the obloid [4<sup>4</sup>5<sup>4</sup>6<sup>4</sup>8<sup>4</sup>] cage of ITQ-12. In this plane, the SDA molecule

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**Figure 6.** Refined unit cell of as-synthesized ITQ-12 viewing down the  $z$  axis, showing the locations of fluoride ions inside the distorted double 4-ring and 1,3,4-trimethylimidazolium ions in the  $[4^4 5^4 6^4 8^4]$  cage.

aligns with its longest dimension approximately along the long axis of the ellipsoid, which points along [010]. The methyl groups are pointing toward the regions with 6- or 8-ring windows. Each cage occludes one TMI that fits well the dimensions and the slit shape of the cage, especially in the  $x$  direction (i.e., in the smallest dimension of both the cage and the cation); given that the equatorial plane of the zeolite cavity is approximately normal to the  $x$  axis, the larger  $a$  parameter in the as-made sample suggests a tight fit of the flat aromatic cation inside the slit-shaped cavity. The Si–Si average distance in the D4R separating adjacent cavities along the  $x$  direction increases from 3.05 to 3.12 Å upon calcination, while the  $a$  cell parameter becomes smaller; it appears that the TMI cation is “pushing” the cavity walls outward, thus increasing its thickness.

The confinement of the SDA in the ITW cage has been analyzed by measuring the distances from the carbon atoms to the framework oxygen atoms (see Supporting Information). From this analysis, a close fit of the SDA not only in the [100] but also in the [010] direction is apparent, since all the distances in those directions are very close to or smaller than the sum of the corresponding van der Waals radii, which takes into account the methyl hydrogen atoms and C–H···O hydrogen bonds. Along [001], which is the direction of the open channel, the template is less confined.

**Structure-Direction in the Synthesis of ITQ-12.** The exact function of SDAs in the crystallization of zeolites under hydrothermal conditions is still poorly understood, and the case of ITQ-12, considering the structure of its as-synthesized form, is indeed very interesting in this respect. Structure-directing agents of two kinds (the fluoride anion and the organic cation) need to be considered.<sup>26</sup>

First, as already pointed out, pure silica zeolites with D4R units have never been synthesized in the absence of fluoride anions, and in all cases in which the unit has been found, the fluoride ion has been shown to reside inside that unit. This certainly points to structure-direction by the fluoride ion.

Second, organic cations are typically used in the synthesis of high silica zeolites, playing roles that range from mere space fillers to true templates and that could generally be referred to as structure-directing agents of different strength and specificity.<sup>27</sup> In this view, true templates show a strong and highly specific structure-direction related to a favorable host–guest interaction and a close geometric matching between the SDA and the void space in which it is accommodated in the zeolite. True templates are thus expected to direct the synthesis toward a single zeolite structure in a wide range of synthetic conditions and framework compositions. Specificity is also expected to require a high conformational rigidity and a definite size and shape of the cation.<sup>22,28</sup> These requirements are nicely met by 1,3,4-TMI, with a planar, rigid aromatic ring and three methyl substituents with no conformational freedom other than the rotation around the C–C or C–N bonds out from the ring.

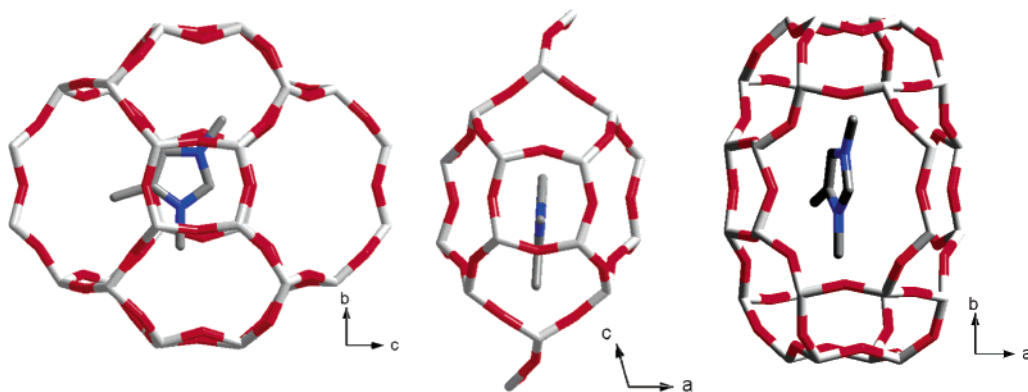
The close fit and correspondence between 1,3,4-TMI and the cage in which it is accommodated tempt us to consider this cation as a true template. However, there are two objections against a “true templating effect” as defined above. First, the effect is not robust enough to ensure that 1,3,4-TMI alone will direct the crystallization of ITW: for instance, in certain syntheses (for which we deem likely HF was not homogeneously distributed throughout the gel), other zeolites (like ZSM-22 and -23) compete. Second, another small, rigid, and planar SDA (the 1,2,3-trimethylimidazolium), which is very similar to but slightly different than 1,3,4-TMI, also promotes the synthesis of ITQ-12.<sup>9,10</sup> Since 1,2,3-trimethylimidazolium and 1,3,4-trimethylimidazolium can both be occluded in that cage and they are not exactly identical in shape, although they are certainly quite similar, it is not possible to claim that either of them presents a perfect geometric match with the size of the void space in the cage: a truly perfect match of one would prevent the other from being accommodated in the same void space. Figure 8 shows the locations of 1,3,4- and 1,2,3-TMI cations in the framework model of ITQ-12 as simulated using Cerius<sup>2</sup> (via a Monte Carlo method and not a molecular fitting). The simulated position of 1,3,4-TMI is identical with the synchrotron XRD result discussed above; i.e., the cation lies in the plane parallel to the  $[4^4 5^4 6^4 8^4]$  cage slit, with one methyl group pointing to an 8-ring window and the other two methyl groups pointing to 6-ring windows. 1,2,3-TMI occupies the same plane, with the methyl groups pointing to the 8- or 6-ring windows as well, showing that, despite the slightly different shape, it can also nicely fit into the cavity. Comparison of the two drawings shown in Figure 8 suggests that 1,2,3-TMI fits the cage as well as 1,3,4-TMI, i.e., very tightly along [100] and [010] and somehow more loosely along the [001] channel. Along [100] and [010], both isomers present the same features: a flat aromatic ring with two methyl groups in 1,3 relative positions, yielding a highly constrained arrangement. A single methyl group is pointed in the [001] direction, affording a looser fit of the SDA along the channel direction. Finally, for both aromatic cations, the positive charge should be quite delocalized by resonance, although a higher charge density may be expected on the N atoms, which in both cations occupy similar positions within the cage (Figure 8) and have identical substituents. From this comparison, we can conclude also that both isomers can

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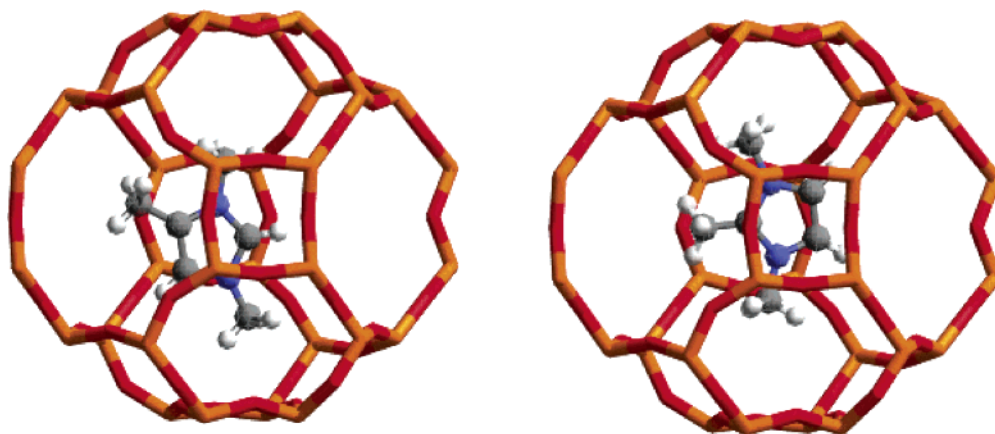
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**Figure 7.** Location of 1,3,4-trimethylimidazolium cation in the cage of ITQ-12 as found by synchrotron X-ray diffraction and Rietveld refinement in the space group  $Cm$ , viewed down the  $x$ ,  $y$ , and  $z$  axes, respectively.



**Figure 8.** Location of 1,3,4- (left) and 1,2,3-trimethylimidazolium (right) cations in the cage of ITQ-12 as simulated using Cerius<sup>2</sup>, viewed down the  $x$  axis.

act as good SDAs for ITW because both fit closely and similarly the shape of the ITW cage.

An additional third objection with regard to specificity is that when the 1,2,3-TMI cation was used in the absence of fluoride ions, ZSM-12 (a large pore zeolite) was obtained,<sup>29</sup> again indicating a lack of robustness and specificity in the structure-direction properties of these cations. Thus, since pure silica materials with the D4R unit have never been synthesized without the aid of fluoride ions and silica ITQ-12 also requires the use of fluoride, it appears that the crystallization of ITQ-12 is the successful result of the cooperative structure-directing effects of  $F^-$  and  $TMI^+$  ions.

## Conclusions

The proposed topology of calcined ITQ-12 has been confirmed, and the detailed structure in space group  $Cm$  has been satisfactorily refined by use of synchrotron powder diffraction data. The choice of a space group lower than the maximum topological symmetry ( $C2/m$ ) is fully supported by <sup>29</sup>Si MAS NMR. The presence of slit-shaped  $[4^45^46^48^4]$  cages with a small-pore entrance close in size to the cross section of propene and propane is relevant to the reported molecular sieving behavior of ITQ-12, which is an efficient and attractive adsorbent for the separation of these chemicals from their mixtures.

The structure of as-synthesized ITQ-12 has been also solved and shown to have fluoride anions in the slightly distorted double 4-ring cavities as well as 1,3,4-trimethylimidazolium cations in the large  $[4^45^46^48^4]$  cage. The flat, rigid, and small cation, modeled as a rigid body, lies in the equatorial plane of the slit-shaped cage and fits tightly in the cage along  $[100]$  and  $[010]$  and more loosely along  $[001]$ . Both the  $F^-$  anion and the  $TMI^+$  cation appear to be necessary for the crystallization of ITQ-12, pointing to a cooperative structure-directing effect.

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**Supporting Information Available:** Bond lengths and angles of calcined and as-synthesized ITQ-12 refined in the space group  $Cm$ ; closest interatomic distances between 1,3,4-trimethylimidazolium and the ITW  $[4^45^46^48^4]$  cage as refined in the space group  $Cm$ ; Rietveld refinement conditions, resulting atomic positions, bond lengths, and angles for calcined and as-synthesized ITQ-12 in the space group  $C2/m$  (PDF); four X-ray crystallographic files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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