

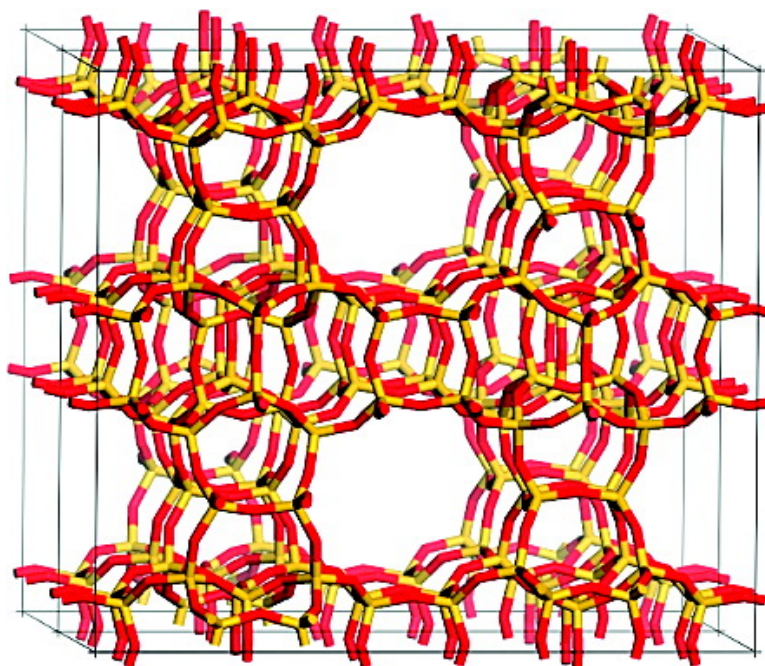
Communication

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## A Zeolitic Structure (ITQ-34) with Connected 9- and 10-Ring Channels Obtained with Phosphonium Cations as Structure Directing Agents

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Zeolites with pores of different dimensions within the same structure can present specific catalytic properties derived from the possibilities of performing molecular traffic control<sup>1</sup> when reactants and/or products of different molecular dimensions could react and diffuse. Some examples of zeolites with pores of different sizes within the same structure are SSZ-51,<sup>2</sup> MCM-68,<sup>3</sup> ITQ-22,<sup>4</sup> IM-12,<sup>5</sup> ITQ-15,<sup>6</sup> and ITQ-33.<sup>7</sup> Special mention requires the zeolite ITQ-13 (ITH), whose structure was solved from single crystal diffraction data, and presents a system of pores by  $9 \times 10 \times 10$  rings, with pore diameters of  $4.0 \text{ \AA} \times 4.9 \text{ \AA}^2$ ,  $4.8 \text{ \AA} \times 5.7 \text{ \AA}^2$ , and  $4.7 \text{ \AA} \times 5.1 \text{ \AA}^2$ , respectively.<sup>8</sup> Because of its peculiar pore system it presents excellent catalytic properties for producing propylene when used as a FCC additive<sup>9</sup> as well as for toluene disproportionation.<sup>10</sup>

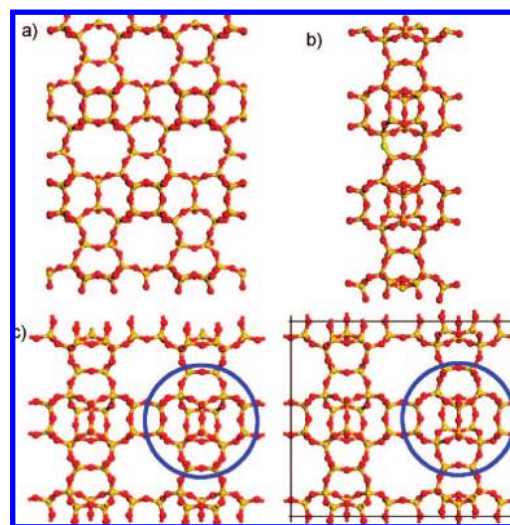
ITQ-13 zeolite was synthesized<sup>11</sup> with hexamethonium [hexane-1,6-bis(trimethylammonium)] as structure directing agent (SDA). We have seen that the ITH structure can have at least one hypothetical polymorph (polymorph B, now on named ITQ-34) that can also be described as a stacking of zeolitic sheets connected forming double four-rings (D4R). However, while in the case of ITQ-13 (polymorph A), these sheets extend in the *bc* plane and stack along the *a* direction with a stacking sequence AAA...; in the case of ITQ-34 the stacking sequence is ABAB..., where B corresponds to the A sheet of ITQ-13 after applying a 180° rotation around the *b* axis and a translation of  $1/2$  along the *c* axis. Then, the cell axis of both polymorphs will be closely related, the *b* and *c* axis being identical because of the common basic sheet. The *a* axis of ITQ-34 will be double of that in ITQ-13 because of the different stacking sequence (ABAB... vs AAA...). However, to adopt a standard setting for the space group expected for ITQ-34 (*Cmcm*), the cell axis of ITQ-34 will need to be defined as  $a_{(\text{ITQ-34})} = b_{(\text{ITQ-13})}$ ,  $b_{(\text{ITQ-34})} = c_{(\text{ITQ-13})}$ , and  $c_{(\text{ITQ-34})} = 2a_{(\text{ITQ-13})}$  (Figure 1). Also, both structures will have an identical framework density of 17.4 T atoms per 1000 Å<sup>3</sup>.

If one simulates the structure of ITQ-34 it can be seen by simple docking that hexamethonium could, in principle, be an adequate SDA for the synthesis of this material. More specifically, when a computational approach (see Supporting Information) has been applied to calculate the short-range Van der Waals (E1) and the electrostatic (E2) interactions between the optimized zeolite-SDA system for ITQ-13 and ITQ-34 and hexamethonium, it is possible to see (Table S1 in Supporting Information) that this SDA orientates slightly better toward ITQ-13 than to ITQ-34. Then, when exploring the experimental synthesis conditions in a wide range of gel compositions using hexamethonium as SDA we found that in no case was the pure ITQ-34 obtained, but mixtures of ITQ-13 and

ITQ-34 were recovered. A closer analysis of the short-range (E1) and long-range (E2) zeolite-SDA contributions (Table S1 in Supporting Information) indicates that, while the short-range energetic contributions are the same for both structures, the electrostatic term SDA-F is less favorable for ITQ-34. Therefore, for achieving a better electrostatic interaction we thought of using shorter dicationic chains such as ethane-1,2-, propane-1,3-, and butane-1,4-bis(trimethylammonium) (di-, tri-, and tetramethonium, now on NC2N, NC3N, and NC4N), as well as the corresponding bis(trimethylphosphonium) cations (PC2P, PC3P, and PC4P), since those have been very successful for synthesizing new structures.<sup>12</sup>

Experimentally we have found that NC2N, NC3N, NC4N, and PC4P cations do not lean toward the synthesis of either ITQ-13 or ITQ-34, while PC2P and PC3P yield pure ITQ-34, the synthesis being faster with the second one. Theoretical calculations with NC3N and PC3P as SDA were performed as above, and results in Table S1 show that with the PC3P cation as SDA short and long-range interactions are clearly more favorable for ITQ-34 than for ITQ-13. This could explain why the pure ITQ-34 could be obtained with the PC3P cation. However, what we can not explain is why NC3N did not lead into the ITQ-34 though it can also better stabilize ITQ-34 than ITQ-13.

In any case, we can say that pure ITQ-34 can be obtained in fluoride medium, using propane-1,3-bis(trimethylphosphonium) (PC3P) as SDA, and a Si/Ge ratio of 10 in the synthesis gel,<sup>13</sup> as it is described in the Supporting Information.



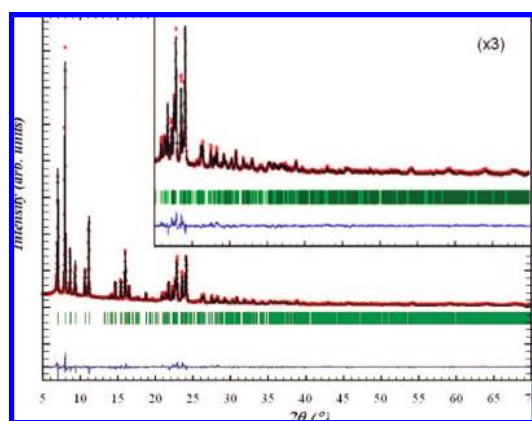
**Figure 1.** (a) Basic sheet of the ITQ-13 (view along [100]) and ITQ-34 (view along [001]) zeolites. (b) Basic sheet of ITQ-13 (view along [010]). (c) Stacking sequences in ITQ-13 (left) and ITQ-34 (right). The blue circles highlight the differences in the stacking of the zeolitic sheets.

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$^{13}\text{C}$  and  $^{31}\text{P}$  MAS NMR spectra of the noncalcined material indicated that the SDA remained stable after the synthesis, and  $^{19}\text{F}$  MAS NMR suggested the presence of F atoms in D4R and  $45^26^2$  units, as described for ITQ-13.<sup>14</sup>

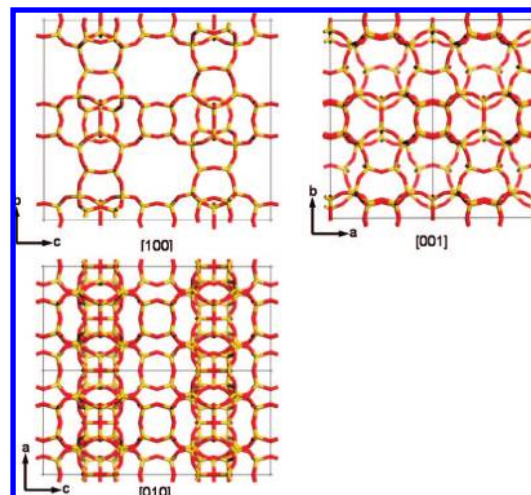
The X-ray powder diffraction pattern of calcined ITQ-34 was indexed in an orthorhombic unit cell with  $a = 11.509 \text{ \AA}$ ,  $b = 22.173 \text{ \AA}$ , and  $c = 25.256 \text{ \AA}$  using the program TREOR,<sup>15</sup> and the analysis of systematic extinctions suggested the possible space groups  $Cmc_2$  (No. 36),  $C2cm$  (No. 40) or  $Cmcm$  (No. 63). Then, the crystal structure was solved using the program FOCUS<sup>16</sup> with the highest symmetry ( $Cmcm$ ). Two possible frameworks were obtained and, after checking both of them, the first structure was found to be the right one, being also coincident with that expected for this polymorph. Then, oxygen atoms were placed between the tetrahedral atoms, and the structure was geometrically optimized using the program DLS-76.<sup>17</sup> Finally, a Rietveld refinement was performed using the program FULLPROF.<sup>18</sup> The residuals of the refinement were  $R_{\text{exp}} = 0.062$ ,  $R_{\text{wp}} = 0.120$ ,  $R_{\text{f}} = 0.063$ , and  $R_{\text{B}} = 0.063$ . The agreement between observed and calculated patterns is shown in Figure 2. Rietveld refinements in lower symmetry groups did not produce an improvement in the refinement.



**Figure 2.** Rietveld refinement of the X-ray diffraction pattern of ITQ-34 calcined at 823 K. Observed (red) and calculated (black) XRD patterns, as well as difference profile (blue) are shown. The green short tick marks below the pattern give the positions of the Bragg reflections.

The channel system of the new zeolite ITQ-34 can be described as three-dimensional combination of three different channels. The first one is formed by 10-ring straight channels along the  $a$  axis, with pore diameters of  $6.03 \text{ \AA} \times 4.87 \text{ \AA}$ . The second one consists in a circular 10-ring channel system lying in the  $ab$  plane, with pore openings of  $5.25 \text{ \AA} \times 4.73 \text{ \AA}$ . Finally, the third pore system is formed by short alterned 9-ring channels along the  $c$  axis, with apertures of  $4.86 \text{ \AA} \times 4.12 \text{ \AA}$ , and interconnecting the other channel systems (Figure 3, and Figure S7 in the Supporting Information). This pore system is in very good agreement with the results obtained from Ar and  $\text{N}_2$  adsorption isotherms obtained at 87 and 77 K, respectively. The calculated micropore volume is  $0.15 \text{ cm}^3/\text{g}$  and the pore aperture is  $5.6 \text{ \AA}$  for ITQ-34.

The structure of calcined ITQ-34 contains nine symmetrically independent T-sites, and Rietveld refinement of the XRD pattern indicates the preferential isomorphous replacement of Si atoms with Ge in positions corresponding to the D4R (sites T4 and T5, with 28 and 26% Ge, respectively), a lower Ge occupancy in sites T7, T8, and T9 (9, 10, and 7% Ge, respectively), and positions T1, T2, T3, and T6 being purely siliceous. This preferential occupation of the D4R is typical in Ge-containing zeolites, as previously reported for other materials.<sup>19,20</sup> The chemical composition obtained from



**Figure 3.** Structure of zeolite ITQ-34 viewed along the three crystallographic axes (red, oxygen; yellow, silicon/germanium).

the refinement is  $[\text{Si}_{0.91}\text{Ge}_{0.09}\text{O}_2]$ , which closely matches that obtained by chemical analysis  $[\text{Si}_{0.90}\text{Ge}_{0.10}\text{O}_2]$ .

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**Supporting Information Available:** Theoretical calculations, synthesis procedure, NMR data, XRD data collection conditions, table of atomic coordinates, table of interatomic distances and angles, and an X-ray crystallographic (CIF) file of atomic coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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