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Synthesis and Structure Determination of a New Microporous Zeolite with Large Cavities Connected by Small Pores

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Ⓢ *Supporting Information*

ABSTRACT: A new small-pore germanosilicate zeolite, named as ITQ-49, has been synthesized using a new ditetraalkylphosphonium dication as an organic structure-directing agent, and its structure has been solved by direct methods applied to the powder X-ray diffraction pattern of the calcined solid. This new zeolite crystallizes in the space group *Immm* with cell parameters $a = 19.6007(8)$ Å, $b = 18.3274(7)$ Å, and $c = 16.5335(6)$ Å. The pore topology of ITQ-49 consists of large, nonspherical cavities that are connected to each other through small eight-membered-ring windows, resulting in a unidirectional small-pore zeolite that has a relatively large adsorption capacity. Also, ITQ-49 contains double four-membered-ring units where Ge is preferentially located, and fluoride anions are placed inside these units.

Zeolites are crystalline microporous materials, mainly constituted by oxides of silicon and/or other elements (e.g., Al, B, Ti, Ge, Sn) in tetrahedral coordination. The well-defined size and distribution of the structural channels in each different zeolitic framework type confer to these materials multiple applications in processes such as gas adsorption, separation, catalysis, and encapsulation or controlled release of molecules, among others, some of them with industrial applications.[1−9] This is the major force for studying novel methods for the preparation of new zeolitic structures, since it would give the possibility of obtaining tailored materials with the most appropriate channel system for each specific application. To date, up to 201 different zeolitic structures have been accepted by the International Zeolite Association,[10] and this number is still increasing.

To obtain novel structures, several approaches have been attempted. The incorporation of fluoride anions replacing hydroxyl anions as the silica-mobilizing agent in the synthesis gel has been found very often to drive the reaction toward the formation of double four-membered-ring (D4R) units in the zeolites obtained under those conditions.[11−21] In the same way, the isomorphic substitution of Si with Ge presents a stronger directing effect, favoring the formation of not only the D4R units[20−30] but also the previously elusive double three-membered-ring (D3R) units,[29,30] opening the doors to new families of zeolites. Nonetheless, the most important approach for obtaining new zeolites is the use of tetraalkylammonium organic cations, which in the zeolite field are generally called organic structure-directing agents (OSDAs).[20,21,31]

Recently, the employment of P-containing OSDAs such as tetraalkylphosphonium and phosphazene cations instead of the tetraalkylammonium cations typically used for zeolite syntheses has been described. These uncommon OSDAs have given several new extra-large-, large-, and medium-pore zeolitic structures.[30,32−35] To date, however, no small-pore zeolites have been synthesized using tetraalkylphosphonium as the OSDA.

In this report, we describe the synthesis and crystal structure of ITQ-49, a new small-pore zeolite containing large non-spherical cavities accessible by a one-directional system of eight-membered-ring (8R) channels, that has been synthesized using ditetraalkylphosphonium dications [obtained from butane-1,4-diylbis(tri-*tert*-butylphosphonium) hydroxide] as the OSDA along with Ge and F^- as inorganic structure directing agents (ISDAs). Details of the synthesis are described in the Supporting Information (SI).

Elemental analysis of the as-made zeolite ITQ-49, as well as ^{13}C and ^{31}P magic-angle-spinning (MAS) NMR spectroscopy (see the SI) indicated that the OSDA dications remain intact within the zeolitic channels, with their positive charges being balanced by the fluoride ions, which are located in the small D4R cages, as indicated by the presence of resonance bands at −9 and −20 ppm in the ^{19}F MAS NMR spectrum of the as-made material[22,36] (see the SI). Chemical analysis showed a Si/Ge ratio of 4.7, very similar to that used in the synthesis gel. The phosphorus content corresponds to a (Si + Ge)/P ratio of 21.6 in the as-made material as well as in the final calcined solid. This indicates that the P-containing OSDA gives rise to the formation of phosphate-like species during calcination, instead of volatile phosphines as occur in zeolites with larger pore apertures. These phosphate-like species were further identified by means of ^{31}P MAS NMR spectroscopy (see the SI). Scanning electron microscopy indicated an average crystal size of ~0.2 μm, precluding structure determination using single-crystal X-ray diffraction.

Powder X-ray diffraction (PXRD) data were collected on a PANalytical X'Pert PRO diffractometer in the Bragg−Brentano geometry using Cu Kα radiation, as described in the SI. Prior to the measurement, in order to remove all of the organic content, the sample was calcined in situ at 923 K for 5 h under a continuous flow of dry air in an Anton Parr XRK-900 reaction chamber attached to the diffractometer.

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The PXRD pattern was then indexed using the program TREOR,[37] which revealed an orthorhombic unit cell with a = 19.6005 Å, b = 18.3272 Å, and c = 16.5333 Å. Analysis of the systematic extinctions suggested as possible extinction symbol I—, corresponding to the space groups $I222$ (No. 23); $I2_12_12_1$ (No. 24); $Imm2$, $Im2m$, or $I2mm$ (No. 44), or $Immm$ (No. 71). Integrated intensities were extracted by a LeBail analysis of the diffraction pattern using the program FULLPROF.[38] The crystal structure was solved using the program FOCUS.[39] As a first attempt, the groups with the lowest and highest symmetries ($I222$, $I2_12_12_1$, and $Immm$) were tested. Only the group with highest symmetry, $Immm$, gave a satisfactory result, consisting in nine independent T (Si or Ge) positions. Next, the positions of 17 bridging O atoms were calculated using the program KRIBER,[40] and the coordinates of all of the atoms were optimized geometrically using the program DLS-76.[41] After a subsequent Rietveld refinement using FULLPROF, this structure proved to be the right one. The PXRD pattern of the refined structure is shown in Figure 1. The residuals of the refinement were $R_{wp} = 0.097$, $R_{exp} = 0.041$, $R_B = 0.057$, and $R_F = 0.093$. Refinements in lower symmetries did not provide any improvement in the residuals.

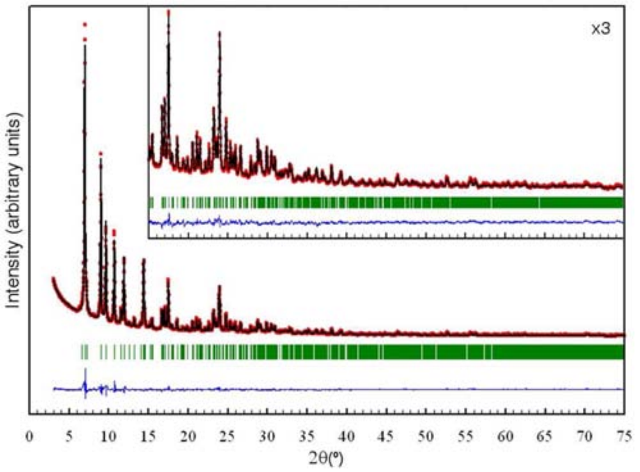

Figure 1. Rietveld refinement of the PXRD pattern of ITQ-49 calcined at 923 K. Data points show the observed PXRD pattern; the line along these points is the calculated pattern, with the difference profile at the bottom. The vertical tick marks below the pattern give the positions of the Bragg reflections. The inset highlights the agreement in the 2θ region from 15 to 75°.

The structure of ITQ-49 can be constructed using four building units (Figure 2). The main cage is a large $4^85^46^87^28^110^1$ unit, which is fused with a second cage by sharing of a 10-membered-ring (10R) window, giving rise to a "peanutlike" large cavity (Figure 2, top right). The structure is completed with nonaccessible $4^86^47^4$, $4^45^46^3$, and 4^6 cages. The "peanutlike" cavities are connected to the neighboring ones by sharing of the 8R apertures, forming straight lobular channels along the b axis that are accessible through the 8R windows with a pore aperture of 5.0 Å × 3.6 Å. However, the entrance to the cavities through the 8R windows is shifted by $b/2$ for each channel relative to its closest neighbors. When the entrance to ITQ-49 zeolite is viewed along the [010] direction, half of the cavities offer an 8R pore aperture, while the other half present a 10R cup corresponding to a hemicavity (Figure 3, bottom).

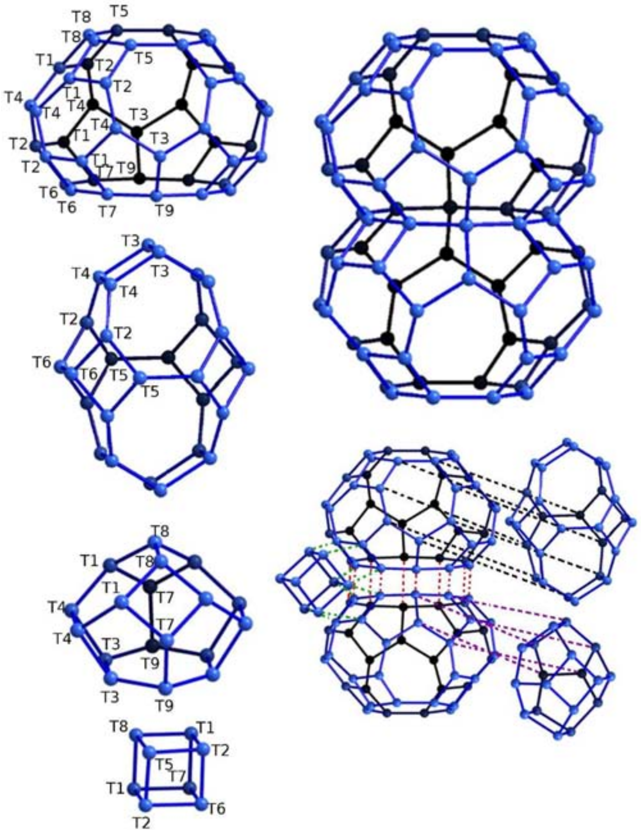

Figure 2. Building units of ITQ-49, indicating the constituting T atoms. Left, from top to bottom: $4^85^46^87^28^110^1$, $4^86^47^4$, $4^45^46^3$, and 4^6 units. Right: top, "peanutlike" cavity with 7R and 8R entrances; bottom, relative location of the cages. Oxygen atoms have been omitted for clarity.

The presence of the odd seven-membered-ring (7R) units is very unusual in zeolites, and only other four structures, ZSM-18 (MEI),[42] SSZ-58 (SFG),[43] SSZ-23 (STT),[44] and VPI-8 (VET)[45] present this type of ring. In fact, ITQ-49 is the first small-pore zeolite having 7R units in its structure. Each 7R window has a pore opening of 3.7 Å × 2.2 Å, which is too small to allow diffusion of any relevant molecule for catalysis or separation. Thus, this topology must be considered as a unidirectional 8R zeolite rather than a bidirectional 7R × 8R zeolite.

The structure of zeolite ITQ-49 is fully consistent with the adsorption properties. The micropore volume estimated from the N_2 adsorption isotherm at 77 K is 0.18 $cm^3\ g^{-1}$. The average micropore aperture calculated from the high-resolution Ar adsorption isotherm at 87 K is 6.1 Å, which is much larger than that obtained from crystallographic data. However, this discrepancy can be explained considering that the 8R windows give access to very large cavities, resulting in overestimated pore aperture values, as observed previously for other well-known zeolites.[46]

The use of Ge and F^- as ISDAs during zeolite crystallization leads to the presence of D4R units in the ITQ-49 framework. Notoriously, the D4R cages in this structure possess the lowest symmetry reported to date for this building unit, with six independent T sites (Figure 2). This allowed us to perform a detailed study of preferential Ge occupation among the different T sites.

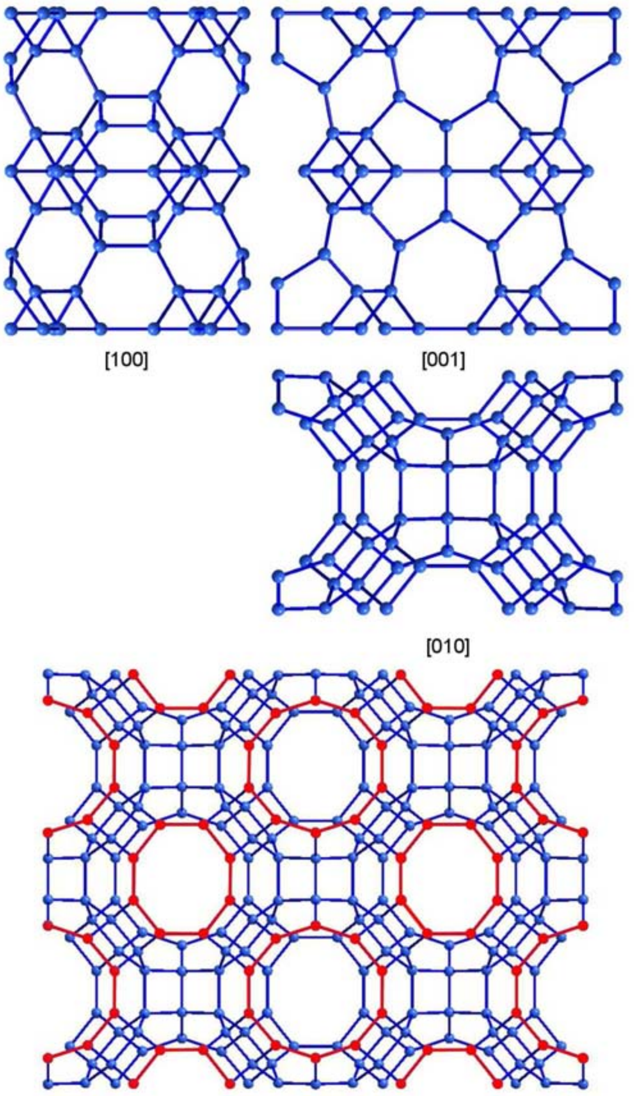

Figure 3. Structure of zeolite ITQ-49. Top and center: views along the main crystallographic axis [100], [010], and [001]. Bottom: distribution of the 8R channels along [010]. The outermost shell of T atoms placed at the channel apertures are highlighted in red. Oxygen atoms have been omitted for clarity.

Rietveld refinement of the T-site occupancies as a mixture of Si and Ge indicated a total Si/Ge ratio of 4.7, in good agreement with the chemical analysis. The preferential occupation of Ge at T6 sites (Si/Ge = 2.0) is clear, with smaller Ge occupancies at T1, T2, T7, and T5 (Si/Ge = 3.6, 3.4, 3.5 and 5.2, respectively); all of these sites are located in the D4R cage. On the other hand, there is a clear preferential occupation of Si at T8 sites (Si/Ge = 9.2), which are also placed in the D4R units. This value is very close to that observed in T sites not in the D4R cage. This is clear evidence that there is a large chemical anisotropy inside the otherwise highly symmetrical D4R cage.

The occupancies of Ge at T9 sites (Si/Ge = 12.9), corresponding to the first neighbor of the D4R unit, and at T3 (Si/Ge = 8.3) and T4 (Si/Ge = 10.9) sites in a single four-membered ring are also low. All of these values are in good agreement with the behavior previously described for other zeolitic silicogermanates.[22−30]

Therefore, we can conclude that the use of new ditetraalkylphosphonium dications as the OSDA combined with the use of Ge and F^- as ISDAs during zeolite crystallization has resulted in a new unidirectional small-pore zeolite, which we have named ITQ-49.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Syntheses of the OSDA and the zeolite; characterization by chemical analysis, thermal and textural analysis, solid-state MAS NMR spectroscopy, and PXRD; atomic coordinates of ITQ-49 and a table of interatomic distances and angles; and a CIF file of atomic coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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