

## Synthesis of Silicate Zeolite Analogues Using Organic Sulfonium Compounds as Structure-Directing Agents

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**Abstract:** A microporous crystalline silica zeolite of the MEL structure type and three other zeolite analogues composed of germanosilicate frameworks were synthesized using tributyl-sulfonium, triphenylsulfonium, or tri(para-tolyl)sulfonium as the structure-directing agent. The germanosilicates thus obtained had ISV, ITT, or a new zeolite structure depending on the synthesis conditions. The structure of the new germanosilicate was solved using X-ray powder diffraction data with the aid of a charge-flipping method. The solution indicated a crystal structure belonging to the P63/mmc space group with cell parameters of a = 16.2003 Å and c = 21.8579 Å. After calcination, the new germanosilicate material exhibited two types of accessible micropores with diameters of 0.61 and 0.78 nm.

Leolites and zeolite analogues are a family of crystalline microporous materials, for which more than 220 structure types have been discovered to date.<sup>[1]</sup> Their microporous structures are built of silicate or phosphate frameworks to retain uniform micropores with specific pore shapes, diameters, and connectivity, which depend on the structure type.<sup>[2]</sup> These microporous materials can discriminate adsorbate molecules that are larger than their specific pore apertures. The frameworks can incorporate various elements, which often yield strongly acidic or other catalytic functionalities.<sup>[3,4]</sup> Chemical reactions at these catalytic sites can occur in a shape-selective manner, as the reactants and products should be small enough to diffuse through the pore apertures.<sup>[5]</sup> Owing to the porous textural properties of the inorganic frameworks and their high stability, many zeolitebased catalysts are currently used in oil-refinery and petrochemical processes.<sup>[6]</sup> Many of these applications are still in need of zeolites with new porous textures (i.e., pore shapes and diameters, connectivity, and framework constituents).

The zeolite structure can be controlled by adjusting the synthesis conditions, such as the gel composition or the

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hydrothermal reaction temperature, by using organic structure-directing agents (SDAs), and by crystal seeding.<sup>[7]</sup> Among them, the most versatile method entails the use of SDAs, typically organic ammonium compounds.<sup>[8,9]</sup> The cationic form of the SDAs provides tight electrostatic binding to the silicate anions under hydrothermal synthesis conditions. The SDA cations remain in tight proximity while the silicate anions are polymerized into a three-dimensional zeolite framework. The SDA cations remain embedded in the polymerized silicate framework, stabilizing the metastable, porous zeolite phase. Hence, the choice of SDA is the most important factor affecting the framework topologies of the final zeolite products, although the inverse molecular topologies are not precisely imprinted to the zeolite framework.<sup>[10]</sup> Previous studies have shown that ammonium cations with C/N<sup>+</sup> values between 11 and 15 are the most effective for a variety of high-silica zeolites.<sup>[9]</sup> Cyclic ethers<sup>[11]</sup> and metal complexes<sup>[12]</sup> were also used as zeolite SDAs although they are less common than the ammonium species. Recently, Corma and co-workers synthesized zeolitic materials with new framework structures (e.g., ITQ-27, ITQ-34, ITQ-47, and ITQ-52) using phosphonium,<sup>[13,14]</sup> phosphazene<sup>[15]</sup> and aminophosphonium<sup>[16]</sup> cations. In our work, we explored the possibility of using organic sulfonium compounds as SDAs for the synthesis of zeolites and zeolite analogues. In particular, we focused on the possibility of synthesizing germanosilicates with extra-large pores.

Three organosulfonium compounds (triphenylsulfonium, tri(*para*-tolyl)sulfonium, and tributylsulfonium) were tested for the synthesis of crystalline microporous materials in this study (see the Supporting Information for the synthesis of the organosulfonium compounds and Figure S1 for their molecular structures). The properties of the microporous materials obtained with the sulfonium compounds are summarized in Table 1. Crystalline germanosilicates of three structure types (ISV, ITT, and an unknown structure) could be synthesized using triphenylsulfonium and tri(*para*-tolyl)sulfonium as SDAs in fluoride media. The germanosilicate zeolite analogue with the unknown structure is hereafter referred to as

**Table 1:** Synthesis of crystalline microporous materials using organosulfonium SDAs.  $^{\left[ a\right] }$ 

SDA	Structure type
triphenylsulfonium	ISV
triphenylsulfonium	unknown (GeZA)
tri <i>(para-</i> tolyl)sulfonium	ITT
tributylsulfonium	MEL

[a] Synthesis procedures and detailed results highlighting the effect of the gel composition are provided in Figure S2.

"GeZA". The synthesis of aluminosilicate zeolites was also attempted in basic media without F<sup>-</sup>, similar to conventional zeolite synthesis. However, under these conditions, triphenylsulfonium and tri(*para*-tolyl)sulfonium did not successfully generate microporous crystalline materials. Only tributylsulfonium produced an aluminosilicate zeolite of the MEL structure type (see the Supporting Information for details of its synthesis).

The germanosilicates were synthesized with the following compositions: SiO<sub>2</sub>/GeO<sub>2</sub>/SDA<sup>+</sup>OH<sup>-</sup>/HF/ synthesis-gel  $H_2O = 1:g:0.4:0.4:w$  (molar ratios; g = 0.2-1 and w = 1-15; see the Supporting Information for details). The GeZA germanosilicate was obtained as a pure phase from the following synthesis-gel composition: SiO2/GeO2/triphenylsulfonium/HF/H<sub>2</sub>O = 1.0:1.0:0.4:0.4:1.0 (see the Supporting Information, Figure S3 for an SEM image). Triphenylsulfonium was incorporated within the framework structure of the GeZA product. The SDA content was determined by extracting the organic content with CHCl<sub>3</sub> after dissolution of the as-synthesized material using an HF solution. The CHCl<sub>3</sub> solution was analyzed by <sup>13</sup>C NMR spectroscopy (Figure S4). Furthermore, the C/S molar ratio of the SDA (C/S = 18) was confirmed to be also that of the final GeZA product by elemental analysis.

The powder X-ray diffraction (XRD) patterns of assynthesized and calcined GeZA samples are shown in Figure 1. The XRD patterns were measured with a Cu  $K\alpha_1$ 



*Figure 1.* Powder X-ray diffraction patterns for a germanosilicate zeolite analogue with unknown structure: as-synthesized (bottom) and calcined (top).

radiation source using a SmartLab (Rigaku) diffractometer equipped with a Ge(220) monochromator. The GeZA sample was calcined in two steps: First, N<sub>2</sub> gas was passed over the sample while the temperature was slowly increased to 400 °C and maintained there for four hours. Subsequently, the temperature was decreased to 250 °C, and ozone gas was passed over the sample for two hours. The O<sub>3</sub> calcined sample exhibited the same XRD pattern as the as-synthesized GeZA material, except for the diffraction peak intensities. The Si/Ge ratio was determined to be 1.88 with an inductively coupled plasma optical emission spectrometer. To resolve the framework structure of the as-synthesized GeZA, individual XRD peaks were indexed using the DICVOL, TAUP, and TREOR algorithms. The GeZA materials could be reasonably indexed to having hexagonal symmetry with unit-cell parameters of a = 16.2003 Å and c = 21.8579 Å. By considering the systematic extinction, which depends on the space group, possible space groups could be derived from the powder XRD pattern. The indexing algorithms suggested the *P63/mmc*, *P62c*, and P63*mc* space groups. In contrast to the two-step calcination process, direct calcination of GeZA in air or O<sub>2</sub> at 400 °C resulted in complete loss of the crystalline structure.

The structural details of the GeZA material were successfully extracted from the powder XRD pattern by using the powder charge flipping (pCF) method, assuming the space group to be P63/mmc. In the pCF method, the flipping of low electron density and subsequent Fourier recycling were combined with the histogram matching method to obtain a high-quality electron-density map. From the electrondensity map, most of the atomic positions of the GeZA constituents and a corresponding initial structure model were obtained from least-squares refinements of the distances (Figure S5). The final Rietveld refinement was obtained with a high fitting quality ( $R_p = 6.7 \%$ ,  $R_{wp} = 8.5 \%$ ; Figure S6). The atomic coordinates thus obtained are given in Table S1, and the final crystallographic parameters are given in Table 2. The space group of GeZA was confirmed by analyzing the electron diffraction (ED) patterns. Three-dimensional rota-

**Table 2:** Crystallographic refinement data for the structure of a new germanosilicate zeolite analogue (as-synthesized).

Unit-cell composition	Ge <sub>22.2</sub> Si <sub>41.8</sub> O <sub>128</sub>
symmetry	hexagonal
space group	P63/mmc
a [Å]	16.2003(7)
b [Å]	16.2003(7)
c [Å]	21.8579(4)
$\alpha$ [°]	90
$\beta$ [°]	90
γ [°]	120
cell volume [ų]	4968.0(9)
No. of observation	2082
No. of parameters	119
No. of restraints	70
R <sub>p</sub> [%]	6.7
R <sub>wp</sub> [%]	8.5
R <sub>F</sub> [%]	3.7
GOF	1.67

tion electron diffraction (3D RED) was the best method for this purpose. However, the GeZA material was readily amorphized during the collection of ED patterns. Therefore, it is difficult to collect 3D RED data for GeZA. Instead of the 3D RED technique, we compared the high-resolution TEM images and corresponding ED patterns (or fast Fourier transform diffraction pattern) taken along the [001], [111], and [110] zone axes with the simulated ED patterns (Figure 2). The simulated ED patterns were obtained using the MacTempas program and based on the atomic coordinates given in Table S1. The obtained images are in good agreement with the simulated ED patterns. This result



*Figure 2.* TEM images and their corresponding ED patterns or FFT images for a GeZA sample, which were taken along the a) [001], b) [110], and c) [111] zone axes. The simulated ED patterns of the [001], [110], and [111] zone axes are displayed for comparison.



**Figure 3.** Structure of the organosulfonium-directed new germanosilicate zeolite analogue viewed along the a) *c* axis and b) *a* axis. For clarity, bridging oxygen atoms are omitted.

supported our structure solution obtained by Rietveld refinement of the powder XRD data.

The structure of GeZA can be described as a threedimensional zeolite with extra-large pores and intersecting channels of  $15 \times 12 \times 12$  membered ring (MR) pores (Figure 3). Two 12 MR pores run parallel to the *a* and b axes, respectively, whereas a 15 MR pore runs parallel to the caxis. The 15 MR pore is an extra-large and oddnumbered ring pore, which has not been observed in aluminosilicate zeolite framework before. The germanosilicate ITQ-40 with the IRY structure possesses 15 MR pores,<sup>[17]</sup> but it is not stable when the organic template is completely removed by calcination. The low stability may be attributed to the interrupted structure of ITQ-40, in which one of the Si (or Ge) sites in the unit cell is connected to only three neighboring Si (or Ge) sites. Unlike ITQ-40, GeZA has an uninterrupted structure. This seems to be the reason for its stability after complete removal of the SDA to open the micropores. To the best of our knowledge, the calcined GeZA



*Figure 4.* a) Ar adsorption-desorption isotherm and b) pore-size distribution derived from the adsorption isotherm using NLDFT for the calcined germanosilicate zeolite analogue.

sample is the first example of an open-framework zeolite analogue with 15 MR pores.

The porosity of the calcined GeZA material was analyzed using the Ar adsorption-desorption isotherm obtained at the liquid-argon temperature. As shown in Figure 4, the Ar uptake increased sharply below  $P/P_0 = 0.05$ . Such a sharp increase at very low pressures can be interpreted as the filling of the microporous voids with Ar molecules. The micropore size distribution was derived from the adsorption branch using nonlocal density functional theory (NLDFT). The resulting graph exhibited two peaks centered at 0.61 and 0.78 nm, respectively. The former and the latter corresponded to the 12 MR and 15 MR pores, respectively. Aside from the Ar uptake in the microporous region, another notable increase was observed above a relative pressure of 0.8, which was due to Ar condensation between particles. The calcined GeZA sample exhibited a Brunauer-Emmett-Teller (BET) surface area of  $460 \text{ m}^2\text{g}^{-1}$  and a pore volume of  $0.63 \text{ cm}^3 \text{g}^{-1}$ . However, the calcined sample exhibited a low stability against water vapor. The sample lost more than 50% of its micropore volume after storage in open atmosphere for two months. Unlike the calcined sample, as-synthesized GeZA was stable over the same storage period.

The framework of the calcined GeZA material is constructed of two composite building units (CBUs). The first CBU is composed of 16 tetrahedral (T) atoms with a ring notation of  $[4^35^66^1]$  (Figure S7). The second building unit is a double four-membered ring (D4R) with a ring notation of [4<sup>6</sup>], which has been frequently observed to be a preferential location of Ge in germanosilicates.<sup>[18,19]</sup> All Ge atoms in the GeZA sample are positioned in D4R units. Along the crystal a and b axes, a  $[4^{3}5^{6}6^{1}]$  unit is connected to three D4R units by sharing a 4 MR with a tripod connection, forming a twodimensional layer. The 15 MR pores were regularly arranged with hexagonal symmetry in a two-dimensional layer (Figure 3a). These two-dimensional layers are perpendicularly connected to the adjacent layers by forming four additional T–O–T bonds along the c axes, resulting in the formation of two straight 12 MR channels along the *a* and *b* axes, respectively (Figure 3b).



Tri(*para*-tolyl)sulfonium is somewhat bulkier than triphenylsulfonium. The bulkier SDA generated a microporous crystalline germanosilicate of the ITT structure type from the following gel compositions: SiO<sub>2</sub>/GeO<sub>2</sub>/tri(*para*-tolyl)sulfonium/HF/H<sub>2</sub>O = 1.0:(1.0-g):0.4:0.4:5.0 (g = 0.33-0.5). The ITT germanosilicate is a zeolite with extra-large pores and three-dimensional  $18 \times 10 \times 10$  channels. The micropores in the ITT material could be opened by calcination in air flow at 500 °C (see Figure S8 for the Ar isotherm and the corresponding pore-size distribution). The calcined ITT material had a BET surface area of 520 m<sup>2</sup>g<sup>-1</sup>.

The use of sulfonium compounds as the zeolite SDA was not limited to the synthesis of germanosilicates. Using the hydroxide form of tributylsulfonium, we could synthesize an aluminosilicate (Si/Al = 50) zeolite of the MEL structure type (Figure S9). In this synthesis, the mineralizing agent was the OH<sup>-</sup> anion. The pure silica form of the MEL zeolite was also easily synthesized using tributylsulfonium. However, we could not synthesize any crystalline microporous aluminosilicate zeolites or germanosilicates using trimethyl-, triethyl-, or tripropylsulfonium as the SDA.

In conclusion, we have synthesized aluminosilicate zeolite and microporous crystalline germanosilicate materials using organosulfonium cations as the structure-directing agents. In principle, the structure-directing effect of sulfonium compounds is analogous to that of organic ammonium SDAs in the synthesis of zeolites. However, there is a notable difference in that we can use sulfonium compounds with C/S<sup>+</sup> ratios that are higher than the C/N<sup>+</sup> ratios in the ammonium compounds. This can be attributed to the high polarity of the C-S<sup>+</sup> bond, rendering bulky sulfonium compounds readily soluble in water. The use of sulfonium compounds with a high C/S<sup>+</sup> ratio (i.e., bulky molecular SDAs) could be of particular interest for the synthesis of microporous crystalline materials with extra-large pores ( $\geq$  14 MR). We demonstrated this possibility by presenting a new germanosilicate material that was synthesized using triphenylsulfonium with  $C/S^+ = 18$ . This material exhibited a new open framework structure with  $15 \times$  $12 \times 12$  MR pores.

## **Experimental Section**

Germanium oxide (Aldrich, 99.99%) was dissolved in an aqueous solution containing the hydroxide form of the sulfonium cations. Tetraethoxysilane (TCI, 98%) was added dropwise to the solution under vigorous magnetic stirring. The resultant mixture was stirred at room temperature for 6 h and then freeze-dried. The powder collected after freeze-drying was mixed with a dilute aqueous solution of hydrofluoric acid. The resultant gel was transferred to a Teflon-lined stainless-steel autoclave, and heated with tumbling at 170°C for 6 days. The solid precipitate was filtered, washed with distilled water, and dried at 100°C. The C, H, and S contents of the GeZA sample

were determined using an elemental analyzer (FLASH 2000 series). The Si and Ge contents were determined using an inductively coupled plasma optical emission spectrometer (iCAP 6300 Duo).

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