SCM-25: A Zeolite with Ordered Meso-cavities Interconnected by 12 × 12 × 10-Ring Channels Determined by 3D Electron Diffraction

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ABSTRACT: Zeolites with large cavities that are accessible via wide pore windows are desirable but very rare. They have been dominantly used as catalysts in industry. Here we report a novel porous germanosilicate SCM-25, the zeolite structure containing ordered meso-cavities (29.9 × 7.6 × 6.0 Å³) interconnected by 10- and 12-ring channels. SCM-25 was synthesized as nanosized crystals by using a simple organic structure-directing agent (OSDA). Three-dimensional (3D) electron diffraction shows that SCM-25 crystallizes in the orthorhombic space group Cmmm with a = 14.62 Å, b = 51.82 Å, c = 13.11 Å, which is one of the zeolites with the largest unit cell dimensions. We demonstrate that 3D electron diffraction is a powerful technique for determining the complex structure of SCM-25, including the disorders and distributions of framework atoms silicon and germanium. SCM-25 has a high surface area (510 m²/g) and high thermal stability (700 °C). Furthermore, we propose a potential postsynthetic strategy for the preparation of zeolites with ordered meso-cavities by applying the ADOR (assembly−disassembly−organization−reassembly) approach.

INTRODUCTION

Zeolites are technologically important crystalline microporous materials that have wide applications in catalysis, adsorption/separation, and ion-exchange.1 Their framework structures are built with TO₄ tetrahedra (T= Si, Ge, Al, and B, etc.), which connect to each other through vertex-sharing of oxygen atoms in the tetrahedra. Different arrangements and connections of the TO₄ tetrahedra can form various crystalline structures with tunable chemical compositions and uniform pores and/or cavities of molecular dimensions.2 The microscopic structure features of a zeolite, especially the size and shape of pores/cavities and the dimensionality of channels, significantly govern its macroscopic properties such as size and shape-selectivity and molecular diffusion in catalysis and adsorption/separation.3–5 The search for zeolites with novel framework topologies and unique pore architectures for improved catalysis and adsorption/separation has always been the object of many researches worldwide.

To date, the International Zeolite Association (IZA) has authorized 255 different zeolite framework structures, which can be classified depending on the ring size of pore openings (defined by the number of tetrahedra forming the ring), the dimensionality of channel systems, or the presence of cavities.6 Pores defined by 8, 10, and 12 TO₄ tetrahedra are considered as small pores (8-ring), medium pores (10-ring), and large pores (12-ring), respectively. Among all available zeolites, those with large cavities have been widely applied in many industrial chemical processes and dominate the synthetic zeolite market.6–8 Some examples are LTA (8 × 8 × 8-ring, sphere-like cavity of 10.8 Å in the largest dimension), CHA (8 × 8 × 8-ring, ellipse-like cavity of 9.9 Å), MWW (10 × 10-ring, ellipse-like cavity of 19.0 Å), and FAU (12 × 12 × 12-ring, sphere-like cavity of 13.0 Å). This is because their pore architectures allow both molecular diffusion and shape-selective catalysis/adsorption.7–11 Therefore, zeolites with large cavities interconnected by well-defined pore windows or channels are of great interest.7,12–13 However, studies on these excellent zeolites have shown that their maximum capacities in many applications could still be optimized by increasing the size of pores and/or cavities.14–18

Significant efforts have been made to prepare novel zeolites with unique pore structures, especially those containing extra-large pores (>12-ring, >8.0 Å).19–21 Currently, the main strategies used for preparing zeolites with novel structures are as follows: (i) predesignation of organic structure-directing agent (OSDA), (ii) heteroatom substitution, and (iii) topotactic conversion of 2D to 3D, 3D to 3D, and 3D to 2D materials, including the assembly−disassembly−organization−reassembly (ADOR) approach.22–24 In the past decades, through the strategy of using predesigned large, bulky OSDAs.
and/or heteroatoms, a series of novel extra-large pore zeolites (EMM-23(EWT), ITQ-33(ITT), ITQ-37(ITT), ITQ-40(IRR), ITQ-51(IFO), and ITQ-4531 etc.) have been synthesized, some with pores beyond 20 Å, extending from the microporous range (<20.0 Å) to mesoporous range (20.0−50.0 Å). However, large bulky OSDAs are often difficult to prepare and are expensive, which hinders the applications of those extra-large pore zeolites.22 The ADOR approach takes advantage of the weakness of the structures of germanosilicate zeolites to achieve the selective dissolution of germanium from the structure. It provides the opportunities to prepare novel zeolite families with continuously controllable porosities that are unfeasible by traditional solvothermal synthetic methods. However, so far, the zeolites afforded by ADOR have either irregular mesopores or micropores with reduced pore sizes compared to the parent zeolite.23 Alternatively, mesopores can also be introduced into zeolite crystals via various postsynthetic approaches such as acid, alkaline, and steam treatments.32 However, it is challenging to control the size, shape, and location of mesopores by those treatments. The resulting mesopores are mostly irregular in terms of sizes and distributions, which may sacrifice the crystallinity and shape-selectivity of zeolite materials.11

Zeolites with large cavities that are accessible via large pore windows are desirable, because they allow large molecules to enter the cavities and access the catalytic centers and can also enhance the shape selectivity and molecular diffusion. While the synthesis of zeolites with large/meso-cavities connected to small 8-ring pore windows has been realized in the ABC-6 family,13,33 there is a lack of strategy to synthesize zeolites with ordered meso-cavities accessible via medium (10-ring) and large (12-ring) pore windows. Herein, we report a germanosilicate SCM-25, a zeolite with a hierarchical pore architecture built of meso-cavities fully interconnected by medium and large pores. SCM-25 was first synthesized using a simple and commercially available OSDA in 2019.34 The structure of SCM-25 was determined from nanosized crystals by 3D electron diffraction (3D ED),35−39 more specifically rotation electron diffraction (cRED).40 The framework of SCM-25 is isostructural to that of recently reported HMP-1641 and closely related to that of ITQ-21,42 which has an intersecting 3D 12 × 12 × 12-ring channel system. A potential postsynthesis strategy for preparing zeolites with meso-cavities is proposed based on the structural relationship between SCM-25 and ITQ-21.

## RESULTS AND DISCUSSION

The germanosilicate zeolite SCM-25 was synthesized as nanosized platelike crystals (∼700 × 500 × 30 nm3, Figure S1) in fluoride medium using 1,1,3,5-tetramethyl piperidinium hydroxide (1,1,3,5-TMPOH) as an organic structure-directing agent (OSDA).34 It crystallized from a gel with a molar composition of 0.5 1,1,3,5-TMPOH/0.667 SiO2/0.333 GeO2/0.5 HF/7 H2O at 175 °C for 14 days under dynamic conditions. The detailed descriptions of the synthesis conditions are given in the Supporting Information.

The 13C solid-state MAS NMR of as-made SCM-25 indicates that the OSDAs are intact and accommodated in the structure (Figure S2). The Si/Ge molar ratio of the solid sample is 2.4, as revealed by the inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis (Table S1). In situ PXRD shows that SCM-25 has high thermal stability (>700 °C, Figure S3). Its framework structure was retained after removing the OSDAs by calcination in air at 550 °C (Figure S5). The 29Si solid-state MAS and 1H to 29Si CPMAS NMR spectra of the calcined SCM-25 show that most Si atoms are connected to four TO4 (Q4 species, Si(OT4), T = Si, Ge, Figure S6).28,43 The 19F solid-state MAS NMR spectra of the calcined SCM-25 show that most Si atoms are connected to four TO4 (Q4 species, Si(OT4), T = Si, Ge, Figure S6).28,43 The 19F solid-state MAS NMR spectrum of the calcined SCM-25 show that most Si atoms are connected to four TO4 (Q4 species, Si(OT4), T = Si, Ge, Figure S6).28,43 The 19F solid-state MAS NMR spectrum implies the existence of double 4-ring (d4r) units in the structure (Figure S6).28,43 The N2 adsorption measurements of SCM-25 show a Brunauer–Emmett–Teller (BET) surface area of 510 m2/g with a micropore volume of 0.18 cm3/g (Figure S7).
Meanwhile, a bimodal pore size distribution centered at 6.9 and 8.2 Å was observed (Figure S7).

Because of the nanosize of SCM-25 crystals that are too small for single-crystal X-ray diffraction, continuous rotation electron diffraction (cRED) was used for structure determination of SCM-25 (Figures 1 and 2). cRED data were collected on a JEOL JEM2100 transmission electron microscope (TEM) at 200 kV equipped with a Tixemix hybrid pixel detector using the program Instamatic developed in our lab.40 A cRED data set with 342 diffraction frames and rotation range of 90.61° was collected within 3.4 min (Table S2), which shows that SCM-25 has a large C-centered orthorhombic cell of a = 14.62 Å, b = 51.82 Å, c = 13.11 Å, as identified using the program XDS.45 Based on the reflection conditions observed from the 3D reciprocal lattice reconstructed from the cRED data by the program REDp46 (Figure 2), three possible space groups, Cmmn, Cnm2, and C222, were deduced. Integrated intensities of the reflections were obtained from the cRED data using XDS with a high resolution (0.80 Å) and completeness (89.8%) (Table S2). The framework structure of SCM-25 could be solved with the space group Cmmn using the program SHELXT.47 All the 10 framework T atoms and 24 of 26 framework oxygen atoms in the asymmetric unit were located directly (Figures 1 and S8). While 9 of the 10 T atoms are four-connected, one is three-connected and disordered at two symmetry-related positions. Two terminal O atoms coordinated to the disordered T atom could not be located by SHELXT due to the low occupancy (0.5). They were added based on the geometry of zeolites.

The structural model of SCM-25 was refined against the cRED data using the program SHELXL.49 The highest possible space group Cmmm was applied in the refinement, and the more accurate unit cell parameters obtained from the synchrotron PXRD data were used (Table S3). While all T atoms were refined as mixed Si/Ge sites during the initial refinement, the refinement showed that Ge atoms were mainly distributed in the double 4-ring (d4r) units and the other T-sites were then assigned as Si-site. Restraints on the Si–O bond distances and angles were applied to the disordered terminal Si and O atoms. All atoms were refined anisotropically, and the refinement converged to R1 = 0.1848, wR2 = 0.4388, and S = 1.684 for 2283 reflections with F > 2σ(F) and 286 parameters (Figures 1 and S9, Table S3). The occupancies of Ge atoms and locations of F− ions could be refined without applying any restraints. The Si and Ge compositions of three symmetry-independent d4r units were refined to be Si1.3Ge1.6 (d4r#1), Si1.5Ge1.5 (d4r#2), and Si1.6Ge1.4 (d4r#3) (Figure 1), which are highly consistent with the results revealed by the 39F NMR spectrum (Figure S6) and ICP (Table S1). The refined chemical composition is IF−10[Si94.7Ge41.3O276] (OSDA and H2O molecules were not included in the refinement) and is in good agreement with that ([C64H38F]10.6(H2O)7.8[Si96Ge40.6O276]) calculated from the ICP and TGA analysis (Table S1). The bond lengths are 1.58–1.62 Å (average 1.60 Å) for Si–O and 1.60–1.69 Å (average 1.65 Å) for Si/Ge–O. The T–O–T angles range between 103.3° and 114.9° (average 109.4°), which are chemically reasonable (Table S4). These show the framework structure determined from cRED data is highly reliable. The high R-values are not due to the inaccurate structural model but most likely result from dynamical effects due to multiple scattering of electrons in the crystal and the absence of OSDAs in the model.

Rietveld refinement against the synchrotron powder X-ray diffraction (PXRD) data of as-made SCM-25 was conducted to locate OSDAs in the pores (Figure 3). The framework structure determined by cRED was served as a starting model for Rietveld refinement. During the refinement, the OSDA TMP cations were treated as rigid bodies and located using the simulated-annealing algorithm implemented in TOPAS.
All framework atoms were refined with soft geometric restraints of bond distances and angles. The refinement converged with agreement residuals of $R_{B} = 0.033$, $R_{wp} = 0.170$ with $R_{wp} = 0.099$ (Figure 3 and Table S5). The refined chemical composition is $\left[(\text{C}_2\text{H}_3\text{N})^+\right](\text{F})^{-}$\cdot$(\text{H}_2\text{O})_{0.93}[^{\text{Si}}\text{O}[^{\text{Ge}}]\text{O}_{2.72}]$. The framework structure refined against the PXRD data matches very well with the one refined against the cRED data, with an average deviation in atomic positions by 0.04(2) Å for the T atoms and 0.10(4) Å for the O atoms (Tables S4 and S6). There are 10 TMP\(^+\) cations in each unit cell, which are distributed at four symmetry-independent sites (OSDA\#a, \#b, \#c \#d) with a partial occupancy of 0.158, 0.148, 0.174, and 0.146, respectively (Figure S10).\(^{50,51}\) Their positive charges are balanced by the electron density map (Figure S10), which are found both within and at the pore window of the meso-cavities. Figure S11 illustrates the location of the TMP\(^+\) cations in the meso-cavity.

The framework structure of SCM-25 exhibits a novel topology as elucidated by the crystallographic programs Topos and 3dit.\(^{53}\) The three-dimensional network is composed of nine different tiles (Figure S12). The large complex tile with a face symbol [4\(^{10}\)−6\(^8\)\cdot12\(^4\)] represents the novel shuttle-like meso-cavity in SCM-25, with a size of 29.9 × 7.6 × 6.0 Å\(^3\) (Figures 4a and S12). The shuttle-like meso-cavities are accessible via four 12-ring windows and eight 10-ring windows: two 12-ring (7.6 × 6.8 Å) and four 10-ring (5.4 × 4.7 Å) windows perpendicular to the c-axis, and two 12-ring (8.0 × 6.1 Å) and four 10-ring (5.6 × 5.1 Å) windows perpendicular to the b-axis (Figure 4b and Figure S13). This gives rise to a very open zeolite structure (framework density: 14.7 T/1000 Å\(^3\)) with a unique 3D 12 × 12 × 10-ring channel system built of the ordered meso-cavities interconnected by the medium and large pores. In addition, we found by electron diffraction that the longest direction of the meso-cavity (along the b-axis) is perpendicular to the nanoplates of SCM-25 crystals (Figure S15). These may be beneficial for diffusion, adsorption, and reactivity. The meso-cavities in SCM-25 comprise the unique features of cavities in both FAU (12 × 12 × 12-ring) and MWW (10 × 10-ring) (Figure S14). All these make SCM-25 promising for catalytic and adsorptive applications.

The framework structure of SCM-25 is closely related to that of zeolite ITQ-21 (space group Fm−3c, a = 27.698 Å).\(^{42}\) and both zeolites are built from the same building layer (referred to as ITQ-21 layer) that contains intersecting 12-ring channels along three perpendicular directions (Figure 5). In ITQ-21, the ITQ-21 layers are connected via d4r units to form a 3D framework with the straight 12-ring channels along the a-, b-, and c-axes. In SCM-25, the neighboring ITQ-21 layers are shifted by 1/2a (ca. 7.1 Å) from each other and connected via a tetrahedral pair $O(SiO_2)$−$O(SiO_2)$−$O(SiO_2)$−$O(SiO_2)$. The shift of neighboring ITQ-21 layers blocks the straight 12-ring channels perpendicular to the layer and turns the channels into meso-cavities. From the structural point of view, the framework structure of SCM-25 could be constructed from ITQ-21 via the ADOR approach,\(^{54}\) as illustrated in Figure 5. The assembled ITQ-21 framework is disassembled into ITQ-21 layers by selective removal of every second d4r unit along the b-axis. The ITQ-21 layers are then reorganized by a shift (1/2a) along the a-axis (organization) and connected through tetrahedral pairs (SiO\(_2\)) to form the framework structure of SCM-25 (reassemble). We envisage that the ADOR approach could be used to prepare zeolites with ordered meso-cavities based on the same principle as shown in Figure 5. Kasneryk et al. reported that the unfeasible zeolite IPC-12 could be prepared via the ADOR approach from the parent zeolite UOV which consists of porous layers.\(^{55}\) The d4r units in the UOV framework could be selectively removed to form layers with tunable thickness by tailoring their chemical compositions.\(^{56}\) The layers can be rearranged with a twist to interrupt the straight channels and subsequently reassembled by modifying the ADOR conditions.\(^{57}\) We believe the ADOR approach has also a potential for synthesizing novel zeolites with ordered meso-cavities by simply blocking straight channels in a known zeolite.

It is worth mentioning that SCM-25 is isosstructural to that of recently reported HPM-16.\(^{41}\) While SCM-25 was synthesized using a simple and commercially available 1,1,3,5-TMPOH as the OSDA, the OSDA used for the synthesis of HPM-16, 1-methyl-2-ethyl-3-n-propylimidazolium hydroxide (1M2E3nPrIMOHI), is more complex (Figure 6) and requires...
several steps to produce. While the 3D ED data could only provide an initial model of HPM-16 without considering the distribution of silicon and germanium in the framework, we show that accurate framework structure of SCM-25 including the locations of silicon and germanium atoms could be determined. Meanwhile, by Rietveld refinement against the synchrotron PXRD data, we revealed four symmetry-independent sites of TMP+ cations in SCM-25, which is different from the two symmetry-independent sites of 1M2E3nPrIM+ cations in HPM-16. A comparison of the locations of the OSDAs in the two structures is given in Figure S17. Furthermore, we analyzed the structural relationship between ITQ-21 and SCM-25 and proposed a potential approach to prepare zeolite structures with ordered meso-cavities.

CONCLUSIONS

In summary, we have demonstrated the synthesis and structure determination of a germanosilicate SCM-25, the zeolite containing ordered meso-cavities. SCM-25 was synthesized using a simple and commercially available OSDA and is stable after removing the OSDAs by calcination in air. Recent advances of 3D ED, especially continuous rotation electron diffraction (cRED), made it possible to determine the complex structure of nanosized SCM-25 crystals with high reliability. These are also confirmed by synchrotron PXRD, NMR, ICP, etc. SCM-25 has a unique 3D pore architecture with meso-cavities accessible via large 12-ring and medium 10-ring microporous channels. The high thermal stability together with the unique 3D hierarchical pore architecture makes SCM-25 promising for catalytic and adsorptive applications. In addition, inspired by the structural relationship between SCM-25 and zeolite ITQ-21, we proposed a potential postsynthesis strategy for the preparation of zeolites with ordered meso-cavities.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c03632.

Synthetic procedures, characterization methods and data (3D ED, XRD, SEM, TGA, NMR, etc.), and structure refinement details of SCM-25 (PDF)

Accession Codes

CCDC 2101715–2101716 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Figure 5. Structural relationship between ITQ-21 and SCM-25. The framework structures of these two zeolites share the same porous layers. The framework structure of ITQ-21 is possible to be transformed into the framework structure of SCM-25 via the ADOR approach. This case inspired us to propose a promising approach to prepare zeolites with meso-cavities in their framework structures. O atoms have been omitted for clarity. The corresponding projections viewed along the a-axis are presented in Figure S16.

Figure 6. Molecular structures of 1,1,3,5-TMPOH and 1M2E3nPrIMOH, used as the OSDAs for the synthesis of SCM-25 and HPM-16, respectively.
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