

Microporous Materials

A Stable Extra-Large-Pore Zeolite with Intersecting 14- and 10-Membered-Ring Channels

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Abstract: The development of inorganic frameworks with extra-large pores (larger than 12-membered rings) has attracted considerable attention because of their potential applications in catalysis, the separation of large molecules, and so forth. We herein report the synthesis of the new extra-large-pore zeolite NUD-2 by using the supramolecular self-assembly of simple aromatic organic cations as structure-directing agents (SDAs). NUD-2 is a high-silicon-content germanosilicate with interconnecting 14×10 -membered-ring channels. The SDAs in NUD-2 can be removed by calcination in air at 550 °C to yield permanent pores with a BET surface

Introduction

Extra-large-pore (consisting of more than 12 tetrahedra) zeolites have long attracted the attention of both chemists and industrial entrepreneurs because of their potential applications in the hydrocracking of heavy-oil fractions, the production of fine chemicals, biomass processes, shape-selective catalysis, the separation of large molecules, and so forth.^[1,2] The past decades have witnessed the miraculous development of the synthesis of extra-large-pore zeolites, with more than 16 extralarge-pore silicate-based zeolites reported to date.^[3] However, the synthesis of stable extra-large-pore zeolites remains a challenge.^[4-7]

The recent successful synthesis of extra-large-pore zeolites is mainly due to the use of exotic organic structure-directing agents (OSDAs) and heteroatoms during their synthesis.^[4-7]

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area of 500 m²g⁻¹. Both germanium and organic cations in NUD-2 can also be removed by treatment with acid at lower temperature, thus not only affording recycling of germanium and SDAs, but also providing a highly stable siliceous zeolite. In addition, aluminum ions can be incorporated into the framework of NUD-2. The NUD-2 structure is yet another extra-large-pore zeolite synthesized by using the supra-molecular self-assembling templating approach, thus demonstrating that this approach is a general and applicable strategy for synthesis of new large- and extra-large-pore zeolites.

Rigid bulky OSDAs with the appropriate polarity/hydrophilicity have been shown to be effective in the synthesis of extralarge-pore zeolites, such as the high-silica-content zeolites with 14-membered-ring (14R) pores UTD-1^[8] and CIT-5^[9] and SSZ-61 with 18-membered-ring (18R) pores,^[10] among others. However, bulky OSDAs are usually expensive and not readily available and the preparations of these OSDAs often involve tedious multistep reactions, thus producing low total yields. Moreover, as the size of an OSDA increases, its hydrophobicity often increases, which limits its solubility and diminishes its ability as an OSDA for the formation of zeolites. The presence of heteroatoms such as beryllium, boron, gallium, and germanium during the zeolite synthesis, on the other hand, aids the formation of 3-membered rings (3R) or double-4-membered rings (D4R) and has been deemed to be the key to the synthesis of some of these extra-large-pore zeolites.[4-7] A number of extralarge-pore zeolites have been prepared by using this strategy, for example, OSB-1 (Be; 14R),^[11] SSZ-53 and SSZ-59 (B; 14R),^[12] ECR-34 (Ga; 18R),^[13] IM-12 (Ge; 14R),^[14] GeZA (Ge; 15R),^[15] NUD-1 (Ge; 18R),^[16] PKU-12 (Ge; 20R),^[17] and the ITQ series (Ge; 16R, 18R, 20R, 28R, and 30R).^[18] However, the presence of these heteroatoms in the zeolite frameworks often limited their chemical properties and thermal stabilities that hinder their use as potential catalysts. To address this issue, postsynthetic modification by means of the isomorphous substitution of aluminum or silicon for germanium has been applied to some germanosilicates to yield highly stable aluminosilicate or siliceous zeolites.^[19] Nonetheless, only a few stable extra-large-pore zeolites have been produced so far.

Recently, we prepared an extra-large-pore germanosilicate zeolite NUD-1 with intersecting 18-, 12-, and 10-R channels by using an approach based on the supramolecular self-assembly

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of small aromatic organic cations as SDAs.^[16] The supramolecular-assembly templating (SAT) approach has been noted by others during the synthesis of the high-silica-content zeolite ITQ-29,^[20] the AIPO₄-LTA molecular sieve, and the large-pore AlPO4-5,^[21] in which supramolecular assemblies of aromatic cations occurred and acted as SDAs. This approach can also be applied to the synthesis of the extra-large-pored zeolite ITQ-37.^[22] By using the supramolecular self-assembly of the small aromatic organic cation 1-methyl-3-(2'-methylbenzyl)imidazolium as an OSDA, we recently prepared a new stable extragermanosilicate large-pore zeolite $[Ge_4Si_{28}O_{64}F] \cdot (C_{12}H_{15}N_2)(C_{12}H_{15}N_2F)_{1,20}$, named NUD-2, with intersecting 14- and 10-R channels. The NUD-2 zeolite is a germanosilicate with a molar ratio of Ge/Si as low as 0.1:1, from which the highly stable aluminosilicate and siliceous zeolite NUD-2 can be obtained by postsynthetic modification. It is noted that Boal et al. reported the synthesis of CIT-13 by using a similar synthetic system during the preparation of this report.^[23] The preliminary report by Boal et al. showed that CIT-13 is isostructural to NUD-2. Herein, we report our detailed studies on the single-crystal structure and properties of NUD-2.

Results and Discussion

The NUD-2 zeolite can be synthesized by using either 1methyl-3-(2'-methylbenzyl)imidazolium (SDA1) or 1-methyl-3-(3'-methylbenzyl)imidazolium (SDA2) as OSDAs in the presence of germanium and fluoride ions (see the Experimental Section). The best-crystallized pure phase of NUD-2 was obtained with a gel composition of 1:0.2:(0.75–1):(0.75–1):10 of SiO₂/GeO₂/ SDA(OH)/HF/H₂O at 150 °C for 15 days. Large platelet crystals of NUD-2 suitable for single-crystal X-ray diffraction analysis were obtained for SDA2 (see Figure S1 in the Supporting Information). Figure 1shows the X-ray powder diffraction (XRPD) pattern of the as-synthesized NUD-2, which is in good agreement with the calculated patterns from the single-crystal structural data.



Figure 1. XRPD patterns of a) calcined, b) as-synthesized, and c) calculated NUD-2 based on single-crystal diffraction data. The sample was synthesized from SiO₂/GeO₂/SDA2(OH)/HF/H₂O (1:0.2:1:1:10) at 150 °C for 15 days.

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Single-crystal X-ray diffraction analyses show that NUD-2 crystallizes in the orthorhombic space group C222 with a = 13.762(2), b = 27.452(4), and c = 5.1170(5) Å. The structure of NUD-2 is constructed of two-dimensional sheets and D4R units (Figure 2). The two-dimensional sheets are made of two types of interconnecting parallel one-dimensional zigzag SiO₄ chain along the crystallographical *c* axis. The sheets are perpendicular to the *b* axis and consist of composite building units (CBU) *cas* or *ton* (i.e., 5⁴6² or 5⁴6²8¹ cages, respectively). The sheets are stacked in an ABAB manner along the *b* axis and interconnected by D4R units to form a two-dimensional pore system, with intersecting 14R and 10R channels along the *c* and *a* axes (Figure 2b), respectively.

The NUD-2 zeolite is closely related to the 14R-pore zeolites IM-12^[14] or ITQ-15^[24] (zeolite framework code=UTL) and CIT-5^[9] (CFI), all of which are built on the similar two-dimensional sheets of interconnecting parallel one-dimensional zigzag SiO₄ chains (Figure 2). The two-dimensional sheets are stacked parallel in an ABAB manner and linked to form 14R channels. The sheets in NUD-2 and CIT-5 are basically the same, that is, composed of cas or ton CBUs. In NUD-2, the two-dimensional sheets are linked by D4R units through every other siliconcenter vertex along the caxis to form one-dimensional 14R channels with intersecting 10R channels along the a axis. In CIT-5 (CFI), the two-dimensional sheets are linked by the socalled double zigzag chains (DZCs; parallel to the b axis), thus forming one-dimensional 14R channels along the caxis, with no open channels in other directions. In IM-12 or ITQ-15 (UTL), on the other hand, the two-dimensional sheets are made of two CBUs ton and fer (i.e., a 5⁶6¹ cage), which are linked by D4R units through every three silicon vertexes in two-dimensional sheets to form one-dimensional 14R channels with intersecting 12R channels along the b axis. The pore size of the 14R channel in NUD-2 is 8.3×6.8 Å, which is close to the pore sizes of UTL and CFI (i.e., 9.5×7.1 and 7.5×7.2 Å, respectively). The 10R channel in NUD-2 is elliptical, with a pore size of $3.6 \times$ 6.7 Å. The framework density (FD) of NUD-2 is 16.5 T atoms per 1000 Å³, which is larger than those of UTL (15.2 T), but less than the other 14R zeolites UTD-1, CFI, SZZ-53, and SSZ-59 (17.1, 16.8, 17.9, and 17.8 T, respectively).

The structural refinements of the single-crystal diffraction data showed that the germanium ions in NUD-2 preferentially occupy positions in the D4R units, similar to other gemanosilicate zeolites.^[16] Of the six crystallographically independent Tsites in NUD-2, each T atom (T3 and T4) in D4Rs are 50% germanium and 50% silicon, whereas the other T atoms (T1, T2, T5, and T6) in the layer are basically pure silicon. At the center of each D4R unit, a fluoride ion was located during the structural refinement. Consistently, the solid-state ¹⁹F NMR spectra of the as-synthesized NUD-2 (Figure 3) showed a strong resonance band at $\delta = -7.2$ ppm owing to the fluoride ion present in the D4R. An additional peak at $\delta = -124.0$ ppm in the ¹⁹F NMR spectra is attributed to mobile fluoride ions in the channels, which act as charge-balancing counterparts for the OSDA cations. Solid-state ¹³C NMR spectra of the as-synthesized NUD-2 (see Figure S2 in the Supporting Information) showed that intact OSDA cations were present in the product.

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Figure 2. Structure presentations of NUD-2. a) Two-dimensional sheets made of interconnecting parallel one-dimensional zigzag SiO₄ chains. b) Zeolite NUD-2 is shown to be built upon connections between the layers and D4Rs, thus forming intersecting 14R and 10R channels. c) Zeolite CFI is shown to be built upon connections between the layers and the DZCs, thus forming the 14R channels. d) Zeolite UTL is shown to be built upon connections between the layers and 12R channels. O=red, Si (Ge)=gray or cynan, F=green. The disordered ions in NUD-2 are drawn in one of the two only possible locations.



Figure 3. Solid-state ¹⁹F NMR spectrum of the as-synthesized SDA2-NUD-2. Peaks marked with an asterisk are spin bands.

Thermogravimetric analysis (TGA) showed a weight loss of 17.7% owing to the removal of organic templates (see Figure S3 in the Supporting Information). Based on the crystal-

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structure refinement and analysis by TGA, NMR spectroscopy, and energy-dispersive spectrometry (EDS), the formula of the as-synthesized NUD-2 used for the single-crystal diffraction analyses can be deduced as $[Ge_4Si_{28}O_{64}F]\cdot(C_{12}H_{15}N_2)$ $(C_{12}H_{15}N_2F)_{1.20}$.

Because of relatively high Si/Ge ratio, NUD-2 is stable in a dry atmosphere after calcination at high temperature to remove the organic templates (see the XPRD images in Figure 1). The nitrogen (argon) adsorption of the calcined NUD-2 (see Figure 4 and Figure S4 in the Supporting Information) gave the BET surface area of 357 (500) m^2g^{-1} and a total pore volume of 0.162 (0.228) cm^3g^{-1} . The mean pore size of NUD-2 is about 7.8 Å, obtained by applying the density-functional theory (DFT)^[25] to the argon adsorption isotherm.

It is interesting to note that both the germanium and organic cations in NUD-2 can be removed by treatment with acid, that is, by using procedures that have been applied to some germanosilicates to yield highly stable aluminosilicate or siliceous zeolites.^[19] After the as-synthesized NUD-2 was treated in concentrated hydrochloric acid in the presence of a small amount of tetraethylorthosilicate at 443 K for 24 hours, approximately 76.2% of the organic templates were removed (see Figure S3 in the Supporting Information). Interestingly, the removed organic templates remained intact (see Figure S5 in the Supporting Information), thus suggesting recyclability of these

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Figure 4. Argon-adsorption isotherm of the calcined NUD-2. Insert: the poresize distribution curve based on DFT theory.

templates for zeolite synthesis. More importantly, the structure of NUD-2 after the treatment remained intact (see Figure S6 in the Supporting Information), whereas the germanium content in the samples was significantly reduced; for example, Si/Ge = 8.8:1 in the as-synthesized NUD-2 increased to 50.6:1 after the first treatment (Table 1). Repeated treatment further lowered the germanium content, with the Si/Ge ratio reaching up to 210:1. The degermanated NUD-2 (denoted as NUD-2S) with high Si/Ge ratios was stable after stirring in deionized water for 12 hours (see the XPRD images in Figure S6 in the Supporting Information). It is noted that there were still relatively high concentrations of germanium ions left in the as-made sample with a low Si/Ge ratio of 2.12:1 after two treatments, likely because the germanium ions in these samples reside both in the D4R units and in the layer; the latter are in stable configurations and require further acid treatment to obtain water-stable zeolites with high Si/Ge ratios.^[19] Solid-state ²⁹Si NMR spectra of NUD-2S showed the peaks for the framework tetrahedral silicon atoms between $\delta = -95$ and -120 ppm (see Figure S7 in the Supporting Information), which are similar to the as-synthesized NUD-2 and confirm the stability of NUD-2S. The nitrogen adsorption of the calcined NUD-2S gave a BET surface area of 369 m²g⁻¹ with a *t*-plot micropore surface area of 329 cm³g⁻¹ and a micropore volume of 0.17 cm³g⁻¹ (see Figure S4 in the Supporting Information). Moreover, the aluminum ions, which can generate acidic sites for potential catalytic applications, can be incorporated into the framework of NUD-2 through postsynthetic modification. The ²⁷Al magic-angle spinning (MAS) NMR spectrum of the aluminum-containing NUD-2



Figure 5. Solid-state ²⁷Al NMR spectrum of NUD-2S-Al.

(denoted as NUD-2S-AI; Figure 5) showed a strong signal at $\delta = 51.9$ ppm and a small peak at $\delta = -0.78$ ppm (integal ratio = 16.8:1), which are due to the tetrahedrally and octahedrally coordinated species, respectively. These results suggest that most of the aluminum ions are located in framework positions. Ammonia temperature-programmed desorption (NH₃-TPD) measurements of NUD-2S-AI showed strong desorption peaks in the range 180–250 °C and weak peaks at 280–330 °C (see Figure S8 in the Supporting Information), which are attributed to ammonia chemisorbed at weak and medium acid sites, respectively. In contrast, NUD-2S did not exhibit any significant acidity.

Finally, we note that NUD-2 is another new extra-large-pore zeolite synthesized by using the SAT approach. Although the organic cations in the as-synthesized NUD-2 were not located in the single-crystal structure model due to disorder, the supermolecular assemblies of OSDAs in NUD-2 can be confirmed by means of photoluminescent studies. A dilute solution with the 1-methyl-3-(3'-methylbenzyl)imidazolium (SDA2) monomer weakly emitted at $\lambda = 285$ nm upon excitation at $\lambda = 275$ nm (Figure 6). However, both the concentrated solution of SDA2 and the as-synthesized NUD-2 in solid gave an emission at $\lambda =$ 450 nm (λ_{ex} = 340 nm), which can be attributed to the formation of excimers. The results suggest that the aromatic-containing cations SDA2 formed self-assembled supermolecular aggregates, likely through π - π interactions, during the zeolite synthesis and acted as actual SDAs for the formation of NUD-2. Similar phenomena were observed during the synthesis of ger-

Table 1. Chemical composition and structural properties of as-made and treated NUD-2 zeolites.								
SDA/Si in gel	Ge/Si in gel	Yield [%] ^[a]	Si/Ge in NUD-2	Si/Ge in NUD-2S treated once	Si/Ge in NUD-2S treated twice	Stability in water for $12 h^{[b]}$		
1.5	0.1	68	8.62	48.9	196	stable		
0.75	0.1	64	8.81	50.6	210	stable		
1.0	0.2	50	4.60	20.5	76.4	stable		
1.0	0.2	52	4.54	21.8	82.2	stable		
1.0	0.5	66	2.12	5.3	8.6	unstable		
[a] Based on the Si(Ge) ions. [b] Determined by XPRD.								

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Figure 6. Photoluminescence spectra of the a) dilute $(1 \times 10^{-4} \text{ mol } \text{L}^{-1}, \lambda_{ex} = 275 \text{ nm})$ and b) concentrated (0.3 mol L⁻¹, $\lambda_{ex} = 340 \text{ nm})$ aqueous solution of SDA2OH. c) Solid-state photoluminescent spectrum of the as-synthesized SDA2-NUD-2 ($\lambda_{ex} = 340 \text{ nm}$).

manosilicates ITQ-29,^[20] NUD-1,^[16] and ITQ-37^[22] and aluminophosphates LTA and AIPO-5.^[21] These results show that the SAT strategy is a general and facile approach to synthesize largeand extra-large-pore zeolites.

Conclusion

A new extra-large-pore germanosilicate zeolite NUD-2 has been synthesized by using a supramolecular-assembly-templating (SAT) approach. The NUD-2 network is built on two-dimensional sheets and D4R units, thus forming a two-dimensional interconnecting 14R and 10R channel system. The germanium ions in NUD-2 can be replaced by silicon or aluminum through postsynthetic modification to yield highly stable siliceous or aluminosilicate zeolites. The successful synthesis of NUD-2 has demonstrated that the SAT approach is a general and applicable strategy that has great potential in the synthesis of new large- and extra-large-pore zeolites.

Experimental Section

Materials and methods

X-ray powder diffraction (XRPD) data were collected on a Bruker D8 Advance instrument with CuK α radiation ($\lambda = 1.54178$ Å) at 40 kV and 40 mA with a scanning speed of 0.1 min⁻¹ in the 2θ range 5-50°. Elemental analyses of C, H, and N were performed on an Elemental Vario Micro elemental analyzer. Inductively coupled plasma (ICP) analyses were carried out on a PerkinElmer Optima 3000DV. Thermogravimetric (TG) analyses were performed on a PerkinElmer thermal analyzer in air with a heating rate of 5 Kmin⁻¹. The Micrometrics ASAP 2020 surface-area porosimetry system was used to measure $N_{\rm 2}$ or Ar gas adsorption at 77 or 87 K. SEM/ energy-dispersive spectrometry (EDS) images were obtained on a field-emission scanning electron microanalyzer (Hitachi S-4800) by employing an accelerating voltage of 10 kV. Fluorescence measurements were performed on a FluoroMax-4 spectrofluorometer with slit of 3 nm for excitation and emission. Liquid-state ¹³C NMR spectra were recorded on a Bruker DRX-500 spectrometer. Solidstate NMR spectra were recorded on a Bruker Av-400 spectrometer by using the magic-angle spinning (MAS) technique at room temperature. Solid-state ¹⁹F NMR spectroscopic analysis was carried out at 376.47 MHz in zirconia rotors (diameter = 4.0 mm) at a spinning rate of 14 kHz and the spectra were collected with pulses of 2.1 µs, which correspond to a magnetization flip angle of $\pi/2$ rad and a recycle delay of 10 s. The spectra were referenced to CFCl₃. The ¹³C NMR spectra were acquired at a resonance frequency of 100.62 MHz by using a cross-polarization (CP) MAS sequence with a ¹H NMR excitation pulse of 3.0 µs, contact time of 2.0 ms, a recycle delay of 5 s, and a spectral width of 100 kHz with proton decoupling at 60 kHz spinal64 during acquisition. The $^{\rm 29}{\rm Si}$ MAS NMR spectra were acquired at a resonance frequency of 79.49 MHz with a $\pi/8$ pulse at 56 kHz, spectral width of 100 kHz, and a relaxation delay of 20 s. Solid-state ²⁷AI NMR spectra were recorded on a Varian Unity VXR-400WB spectrometer at 104.2 MHz, with a pulse length of $\pi/18$ rad, a recycle delay of 0.5 s, and a spinning rate of 14 kHz. The NH₃ temperature-programmed desorption (NH₃-TPD) measurements were performed on a micromeritics AutoChem II 2920 chemisorption analyzer. The samples were first treated at 550 °C in an air flow of 50 mLmin⁻¹ for 2 h and then cooled to room temperature, exposed to NH_3 at 100 °C for 90 min, and purged with helium at 50 °C for 5 h to eliminate the physically adsorbed ammonia. Temperature-programmed desorption was conducted by ramping to 450 °C at 10 °C min⁻¹.

The diffraction-data collection for single-crystal X-ray diffraction studies of NUD-2 were carried out on the D8 Venture with Turbo X-ray source with CuK α radiation ($\lambda = 1.54178$ Å) at 296 K, with an exposure time of 30 s in a shutterless mode. The detector distance was 50 mm and the scan width was 0.5°. Data reduction and absorption corrections were performed by using the SAINT and SADABS programs, respectively. The structure was solved by using direct methods with the SHELEX-2014 program and refined with full-matrix least squares on F^2 by using the SHELEX-2014 program. All the organic cations and solvent molecular were not taken into account and squeezed out by PLATON/SQUEEZE. The organic cations were confirmed by elemental analysis and TG measurements. The non-hydrogen ions were refined anisotropically. There were disorders at O10 and O11 in the layer and T3, T4, O7, O8, O9, and F in the whole D4R unit, with each position taking half the occupancies. Details of the crystal parameters, data collection, and refinement results are summarized in Table S2 (see the Supporting Information). The ionic-coordinate data and selected bond lengths and angles are shown in Tables S3-S5, respectively (see the Supporting Information).

Crystal data for NUD-2: Ge₄Si₂₈O₆₄(C₁₂N₂H₁₅F)_{2.2}, M_r =2554.65, platelike crystal, 0.070×0.025×0.005 mm³, orthorhombic, space group *C222*, *a*=13.7618(14), *b*=27.452(4), *c*=5.1170(5) Å, $\alpha = \beta = \gamma = 90^{\circ}$, *V*=1933.2(4) Å³, *Z*=1, ρ_{calcd} =2.194 g cm³, F_{000} =1274, 6717 reflections collected, 1708 unique, (R_{int} =0.0773), final GooF=1.092, R_1 =0.0733, wR_2 =0.1812. CCDC 1474068 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of SDAs

1-Methyl-3-(2'-methylbenzyl)imidazolium chloride (SDA1Cl): 1-Methyl-3*H*-imidazole (8.21 g, 100 mmol) was added to a solution of 2-methylbenzyl chloride (14.00 g, 100 mmol) dissolved in THF (120 mL). The mixture was stirred at 343 K for 2 days. The solvent was removed to yield a viscous oil, which was washed with ethyl ether (3×10 mL) and dried under vacuum overnight (yield=92%).

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The oil was dissolved in water (150 mL) and the chloride organic salt SDA1Cl was converted into the corresponding hydroxide solution by anion exchange. Titration with aqueous HCl (0.1 mol L^{-1}) to determine the final concentration of the hydroxide solution of SDA1OH.

1-Methyl-3-(3'-methylbenzyl)imidazolium cholride (SDA2CI): A similar procedure was used that started from 3-methylbenzyl chloride to obtain SDA2CI (yield = 94%).

Synthesis of zeolites

Zeolite NUD-2 was prepared from the gel with a molar composition of SiO₂/x GeO₂/y SDAOH/yHF/zH₂O, where x = 1-0.04, y = 1-0.5, and z = 3-30 at 423 K for 15 days. A typical synthetic procedure was as follows: germanium dioxide was added to a solution of SDAOH and stirred for 30 min to be dissolved. Tetraethylorthosilicate was hydrolyzed in the above solution. The reaction mixture was mechanically stirred at room temperature for about 2 h, and then a solution of HF (40 wt%) was added. The mixture was homogenized and allowed to reach the desired water ratio by evaporation of ethanol and some water at 80 °C. Finally, the gel was transferred into a steel autoclave with a Teflon-lined vessel (25 mL) and heated at 423 K under static conditions for 15 days. The final powder was filtered, washed with distilled water and ethanol, and dried in air. Table S1 lists the various synthetic parameters that we surveyed when using the designed SDA.

Degermanation of NUD-2

The as-synthesized SDA2-NUD-2 was dispersed in 12 M HCl at room temperature. Tetraethylorthosilicate was this added as a solution was added to the mixture by adding 0.020 mL per 0.1 g of zeolite with stirring for 0.5 h. The mixture was transferred into a Teflon-lined autoclave and heated at 443 K for 24 h. The final powder was filtered and washed with deionized water and acetone (2×). The process was repeated to obtain degermanated NUD-2S.

Alumination of NUD-2

NUD-2S was dispersed in 0.01 M HCl at 363 K. Aluminum sulfate, which was used as the aluminum source, was added to the mixture by adding 15 mg per 0.1 g of zeolite with stirring overnight. The final powder was filtered and washed with deionized water until no aluminum ions were observed with the use of ammonium auritricarboxylate (ATA). The final product was calcined at 823 K to obtain NUD-2S-AI.

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FULL PAPER

Ever expanding: A new extra-largepore germanosilicate NUD-2 was synthesized by using a supramolecular-assembly templating approach. This structure possesses a two-dimensional interconnecting 14- and 10-membered-ring channel system (see figure). The germanium centers in NUD-2 can be replaced by silicon or aluminum atoms by means of postsynthetic modification, thus yielding highly stable siliceous or aluminosilicate zeolites.



Microporous Materials

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A Stable Extra-Large-Pore Zeolite with 🛄 Intersecting 14- and 10-Membered-Ring Channels