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Synthesis of a new molecular sieve using DABCO-based structure-directing agent

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Abstract

A new 1,4-diazabicyclo[2.2.2]octane (DABCO)-based quaternary ammonium compound is designed, synthesized, and used as structure-directing agent (SDA) for molecular sieve synthesis. Several 1,1′-alkylenedi(4-aza-1-azonia-2,5-dimethylbicyclo[2.2.2]octane) type SDAs are used in all-silica synthesis mixtures. Among the SDAs tested, the use of 1,1′-butylenedi-(4-aza-1-azonia-2,5-dimethylbicyclo[2.2.2]octane) gives a new phase (GUS-1), whereas the use of other SDAs gives zeolite beta (*BEA), ZSM-12 (MTW), and ZSM-5 (MFI). The GUS-1 is indexed in the orthorhombic crystal class with refined lattice constants $a = 16.4206(4)$ Å, $b = 20.0540(4)$ Å and $c = 5.0464(1)$ Å. The crystalline architecture of GUS-1 shows the same [0 0 1] projection of the framework as that of mordenite (MOR), and is characterized by a one-dimensional 12-membered ring channel system that is closely related to the channels of ZSM-12. The GUS-1 is stable to heat upon calcination at 700 °C in air. The calcined material exhibits adsorption capacity that is comparable to typical large-pore one-dimensional microporous silicates. The behavior of the SDA during synthesis is also discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Synthesis; Molecular sieve; DABCO; Structure-directing agent; GUS-1

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1. Introduction

Micropores comprised of 12 T-atoms (tetrahedrally coordinated silicon or other atoms) are called large pores [1,2]. Molecular sieves with these pores should have ability to perform catalysis and/or adsorption on organic molecules having large size corresponding to the pore diameter. They can be applied not only as an effective shape-selective catalyst for conversion of relatively bulky organic molecules [3–5] but also as a selective adsorbent and a host material of nanometer-sized clusters. Thus, the synthetic investigation of molecular sieves having large pores and new frameworks is important.

It is well known that organic structure-directing agent (SDA) such as quaternary ammonium cations can assist in the crystallization of high-silica molecular sieves [6–8]. In order to obtain large porosity, it should be the most effective way to use SDA having bulkiness, rigidity, suitable hydrophobicity, and chemical stability under hydrothermal conditions [9]. One of the most suitable structural units for SDA molecule to synthesize large-pore molecular sieve

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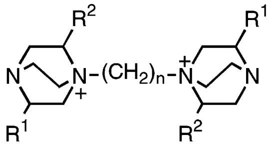
is 1,4-diazabicyclo[2.2.2]octane (DABCO). Several cations derived from DABCO have been used as SDAs for molecular sieve synthesis so far [10–16]. In this work, we designed and synthesized various new DABCO derivatives and used them for molecular sieve synthesis. In particular, we report here the synthesis, characterization, and structure determination of a new microporous molecular sieve (GUS-1) using one of the new SDAs.

2. Experimental

2.1. Synthesis of structure-directing agent

For the synthesis of known cation **1** [10,11], a solution of DABCO and 1,4-dibromobutane (mole ratio 11:2) in acetone was stirred at room temperature for 24 h to give 1,1′-butylenedi(4-aza-1-azoniabicyclo[2.2.2]octane)dibromide (**1**-bromide) in 97% yield. 1,1′-Butylenedi(4-aza-1-azonia-2,5-dimethylbicyclo[2.2.2]octane)dibromide (**7**-bromide), which is a new compound [17], was synthesized as follows: a solution of 1,4-dibromobutane (6.48 g, 30 mmol) in acetone (44 ml) was added dropwise to a solution of 2,5-dimethyl-1,4-diazabicyclo[2.2.2]octane (14.02 g, 100 mmol) in acetone (140 ml) and methanol (30 ml) at room temperature, and the whole mixture was stirred at 70 °C for 70 h. The mixture was filtered and the residue was washed with a mixture of methanol (20 ml) and diethyl ether (200 ml) to give white solid of **7**-bromide (8.54 g, 57.1%). Melting point (mp) 253–260 °C (dec.); ^{1}H NMR (400 MHz, D_2O) δ: 1.27, 1.28, 1.45 and 1.47 (each 3H, s), 1.78–1.95 (4H, m), 2.68–3.72 (24H, m); ^{13}C NMR (100 MHz, D_2O) δ: 15.31, 15.47, 17.59, 17.73, 19.21, 38.65, 46.80, 47.24, 47.94, 49.68, 49.88, 54.15, 54.91, 55.77, 57.85, 58.88, 60.48 and 60.58; IR (neat): 3423 (br), 2974, 1638, 1460, 1400, 1333, 1263, 1246, 1221, 1184, 1136, 1109, 1086, 1065, 1036, 1013, 993, 945, 908, 874, 833, 773, 743, 683 and 565 cm^{-1}.

Each quaternary ammonium dibromide was converted into dihydroxide form with ion-exchange resin and used as the aqueous solution of dihydroxide. Typical procedure of the ion-exchange is as follows: Diaion® SA10A (OH) (Mitsubishi Chemical Co.) anion exchange resin (143.7 g, corresponding to 213 mmol of exchange capacity) was added to a solution of **7**-bromide (20.01 g, 53.2 mmol) in water (200 ml) and the whole mixture was gently stirred at room temperature for 47 h. After filtration, the aqueous solution was concentrated to 79.0 g to give 0.661 mmol/g of **7**-hydroxide based on titration of the resulting solution. The yield was 98.2%. The NMR spectrum of **7**-hydroxide was identical to that of **7**-bromide. Cation **7** was assigned to be an equimolar mixture of four diastereomers.



1 : $R^1=R^2=H$, n=4
2 : $R^1=R^2=H$, n=6
3 : $R^1=R^2=H$, n=8

4 : $R^1=CH_3$, $R^2=H$, n=4
5 : $R^1=CH_3$, $R^2=H$, n=6
6 : $R^1=CH_3$, $R^2=H$, n=8

7 : $R^1=R^2=CH_3$, n=4
8 : $R^1=R^2=CH_3$, n=6
9 : $R^1=R^2=CH_3$, n=8

Fig. 1. Structure of DABCO-based organic structure-directing agents (SDAs) used in this work.

The other SDAs (**2**, **3**, **4**, **5**, **6**, **8** and **9** in Fig. 1) were synthesized by analogous procedures.

2.2. Synthesis of molecular sieve

In a typical synthesis procedure (method A), 4.04 g (1.0 mmol) of **7**-hydroxide solution (0.248 mmol/g), 125 mg of 32 wt.% NaOH solution, and 5.26 g of deionized water were mixed with stirring. The stirring was continued for 15 min and 0.601 g of fumed silica (Cab-O-Sil M-5, Cabot) and 5.80 g of deionized water were added to the homogeneous mixture. The gel was further stirred for 1.5 h to make it completely homogeneous. The molar composition of the gel was as follows: SiO_2:**7**-hydroxide:NaOH:H_2O = 1:0.1:0.1:50. The mixture was then transferred to a couple of quartz tubes (length 75 mm, i.d. 12 mm). About a quarter of the tube volume was left empty and after sealing the tube, they were kept statically in a convection oven at 150 °C for 11–18 days. Afterwards, the tubes were cooled to room temperature and the white crystals were removed from inside by breaking the tubes. Finally, the samples were filtered, washed thoroughly with deionized water and dried overnight to give as-synthesized GUS-1. The GUS-1 sample can also be synthesized in Teflon-lined stainless steel Parr autoclaves.

To remove the organic SDA occluded inside the pore, the as-synthesized sample was kept in a muffle furnace, and heated stepwise in a flow of air (100 ml/min). The temperature was raised from room temperature to 550 °C over a period of 260 min, and maintained at the same temperature for 2 h. The temperature was raised again to 700 °C over a period of 75 min, and kept at this temperature for another 3 h, and finally the sample was cooled to room temperature in ambient condition.

Another method (method B), so-called fluoride method reported by Camblor et al. [18], was also used for the molecular sieve synthesis. The typical procedure was as follows: 10.3263 g of **7**-hydroxide solution (0.2421 mmol/g) was gently stirred in a Teflon vessel. Then 2.1701 g (10.0 mmol) of tetraethylorthosilicate (TEOS, TCI 96%) was added and the mixture was stirred at room temperature for 48 h allowing evaporation of ethanol. To the resulting clear solution, 0.1855 g of HF (55% aqueous solution, Stella Chemifa) was added. The gel became semi-solid after the addition of HF. Water was added to the resultant wet solid to adjust the water content. Manual stirring with a Teflon rod was necessary to make the gel homogeneous. The final composition of the synthesis mixture was as follows: SiO_2:**7**-hydroxide:HF:H_2O = 1:0.25:0.5:10. The gel was divided into two parts and each part was transferred to Teflon-lined stainless steel Parr autoclaves (23 ml each) and heated to 150 °C with rotation (66 rpm) using a convection oven equipped with a rotator. After 14–30 days, the product was recovered by filtration and washed with deionized water, and then dried at room temperature.

2.3. Characterization

The samples were analyzed by powder X-ray diffraction (XRD; Shimadzu XRD-6000 diffractometer, Cu Kα radiation), thermogravimetric analysis (TGA; Shimadzu DTG-50), nuclear magnetic resonance spectroscopy (NMR; Varian Inova 400 or JEOL α-400) and scanning electron microscopy (SEM; Philips XL30 microscope). Nitrogen adsorption measurements were carried out on a BELSORP 28SA gas adsorption instrument.

2.4. Structure determination

The structure of GUS-1 has been determined from synchrotron powder diffraction data of a calcined sample containing the two phases GUS-1 and ZSM-12 [19]. The X-ray data were collected on the beam line X7A at the National Synchrotron Light Source at Brookhaven Laboratory. The sample was loaded in a glass capillary of diameter 1.0 mm. The powder pattern was recorded at room temperature at the wavelength $\lambda = 1.1964$ Å.

3. Results and discussion

3.1. Design and synthesis of structure-directing agent

In the synthesis of high-silica molecular sieves that are somewhat hydrophobic, water-soluble organic molecules, such as quaternary ammonium compounds, can be used as structure-directing agents (SDAs). One approach to the synthesis of large-pore molecular sieves should be through the use of molecule with large dimension [1]. When considering the molecular design, there are some other requirements for organic molecules to function as SDA [7]. The guidelines to develop appropriate SDAs for large-pore molecular sieves are as follows: (1) the molecule is moderately rigid; (2) the molecule is somewhat soluble in both water and silica phases; (3) the molecule has linear shape and a large diameter (especially for molecular sieve with one-dimensional and more than 12-membered ring pore); (4) the molecule is stable under the synthesis conditions of high pH and temperatures higher than 150 °C. On the basis of the guidelines, we planned to modify the structure of DABCO derivative **1** and designed cations **2**–**9** as shown in Fig. 1. Cations **1**–**9** were synthesized by quarternization of corresponding DABCO compounds. If we assume that **1** takes cylindrical shape, then the diameter of **1** is expected to be 0.67 nm (including van der Waals radii).

Table 1
Hydrothermal synthesis using DABCO derivative as SDA

SDA	R^1	R^2	*n*	Product	
				Method A	Method B
1	H	H	4	ZSM-12	Amorphous
2	H	H	6	ZSM-12	Beta
3	H	H	8	ZSM-12	Beta
4	CH_3	H	4	ZSM-12	Beta
5	CH_3	H	6	ZSM-5	Beta
6	CH_3	H	8	ZSM-12	Beta
7	CH_3	CH_3	4	GUS-1[a]	Beta
8	CH_3	CH_3	6	ZSM-5	ZSM-5
9	CH_3	CH_3	8	ZSM-5	ZSM-5[b]

[a] ZSM-12 exists as minor phase.
[b] Beta exists as minor phase.

3.2. Synthesis of molecular sieves

Table 1 shows the results of molecular sieve synthesis using **1**–**9** as SDAs by methods A and B. The XRD patterns for these phases are given in Fig. 2. Difference between methods A and B is described in the Section 2.2. In case of method A and $R^1 = R^2 = H$ (SDAs **1**–**3**), ZSM-12 (MTW) [20,21] readily crystallized independent on the length of methylene bridge ($n = 4$, 6, 8). When $R^1 = CH_3$ and $R^2 = H$ (SDAs **4**–**6**), still there was tendency to form ZSM-12. However, ZSM-5 (MFI) [21] crystallized when $n = 6$, suggesting that the length of methylene bridge is playing some role. When $R^1 = R^2 = CH_3$ (SDAs **7**–**9**), the formation of ZSM-12 was almost overcome, and GUS-1 (when $n = 4$) or ZSM-5 (when $n = 6$, 8) crystallized. Although the GUS-1 was contaminated by ZSM-12, the crystallization of GUS-1 was reproducible. By method B, on the other hand, beta (*BEA) [21] crystallized most frequently; however, ZSM-5 formation became predominant when $R^1 = R^2 = CH_3$.

All phases maintained crystallinity after calcination at 700 °C, indicating the high thermal stability. Next, we focused on the comparison between ZSM-12

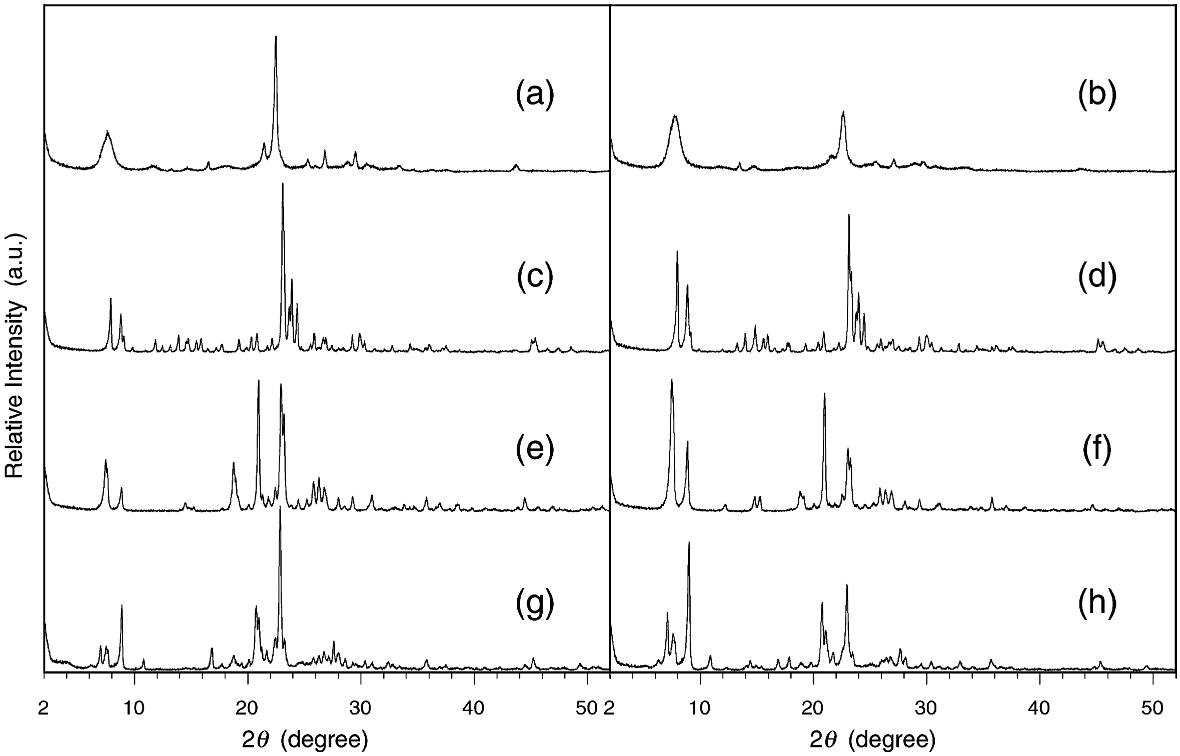


Fig. 2. Powder X-ray diffraction patterns of samples: (a) as-synthesized beta; (b) calcined beta; (c) as-synthesized ZSM-5; (d) calcined ZSM-5; (e) as-synthesized ZSM-12; (f) calcined ZSM-12; (g) as-synthesized GUS-1; (h) calcined GUS-1. GUS-1 is contaminated by ZSM-12.

Table 2
Results from nitrogen adsorption measurements

Sample	Pore volume[a] (cm^3/g)	BET surface area (m^2/g)
ZSM-12	0.129	321
GUS-1	0.107	282

[a] Calculated by *t*-plot method on N_2 adsorption.

and GUS-1. The nitrogen adsorption measurements for calcined ZSM-12 and GUS-1 gave typical type-I isotherms. BET surface areas and pore-volumes were typical for one-dimensional pore systems in both cases as shown in Table 2. Table 3 shows elemental analysis and TGA data for as-synthesized samples. Both elemental analysis and TGA data were consistent with each other; TGA weight loss values were typical of organic contents inside one-dimensional, 12-ring channels of high-silica molecular sieves.

Fig. 3 shows the ^{13}C solution NMR spectra of the SDAs **1** and **7** and ^{13}C CPMAS NMR spectra of as-synthesized ZSM-12 and GUS-1. It was found that **1** was intact inside the pore of ZSM-12 (Fig. 3a and b), whereas **7** partially converted to other organic species in the GUS-1 sample. When the solid NMR of GUS-1 (Fig. 3d) was compared with the solution NMR of **7** (Fig. 3c), disappearance of some peaks (C-1, C-2, and C-3) and appearance of new signals (C-1′, C-2′, and C-3′) were observed. This result may indicate that the Hofmann degradation takes place in the molecule **7** starting from abstraction of the methyl proton at β-position to the ammonium nitrogen. As a result, allylpiperazine unit can be generated (Fig. 3d, inset). The peaks C-1′, C-2′, and C-3′ are assigned to carbons at terminal olefin and allyl position very well. The allylpiperazine-containing unit that is partly formed during hydrothermal synthesis might have caused different structure-directing effect from that by DABCO unit. The formation of allylpiperazine unit is one reason for the lower organic content in GUS-1 than in ZSM-12 as shown in Table 3.

Table 3
Analysis of organic contents in as-synthesized samples

Phase	N^+/Si[a]	Weight loss in TGA[b] (wt.%)
ZSM-12	0.047	10.8
GUS-1	0.027	8.8

[a] Determined by elemental analysis.

[b] Values obtained between 150 and 800 °C at a heating rate of 5 °C/min in air.

The formation of ZSM-12 in the presence of GUS-1 may be partly due to the instability of the SDA **7**. Although the role of methyl groups of **7** in the crystallization process is still unknown, it is clear that the structural modification of SDA affected the structure-directing process in hydrothermal synthesis of molecular sieve.

3.3. Structure determination of GUS-1 [19,22]

We obtained several batches of GUS-1/ZSM-12 mixtures. The approximate proportion of the two phases (GUS-1/ZSM-12) varied in the range 40/60 to 85/15. The particular sample picked up for structure-solution contained the two phases GUS-1 and ZSM-12 in approximate proportion 40 and 60%. The N_2 adsorption isotherms of several GUS-1-containing samples were very similar to the isotherms of pure ZSM-12 samples, suggesting that the GUS-1 phase was also a molecular sieve with 12-ring channels as described in Section 3.2.

Scanning electron micrographs revealed particles of different morphologies. There were two main morphologies of particles. One was needle shaped that is similar to the typical morphology of crystals of ZSM-12. The other was elongated coffin shape. In addition, particles of fan-like shape was observed in the sample which probably correspond to zeolite SSZ-31 as the characteristic (0 0 1) reflection, as trace, was found in the powder pattern at $d = 14.4$ Å [23]. Transmission electron microscopy (TEM) and electron diffraction (ED) investigations showed that the elongated coffin-shaped particle had orthorhombic system.

The powder pattern was indexed using the program TREOR [24], giving an orthorhombic cell with systematic absences consistent with the space group *Cmmm* and subgroups and possibly $C222_1$. GUS-1 possessed a small axis $c = 5.0$ Å, limiting the structure determination to a search of the two-dimensional projection of the zeolite into the *ab*-plane. Models have been built with *Cmmm* symmetry and 12-ring channels running along the *c*-axis. A good candidate was found showing strong similarities to mordenite (MOR). Additional searches were performed using the program FOCUS [25,26]. The structure factors

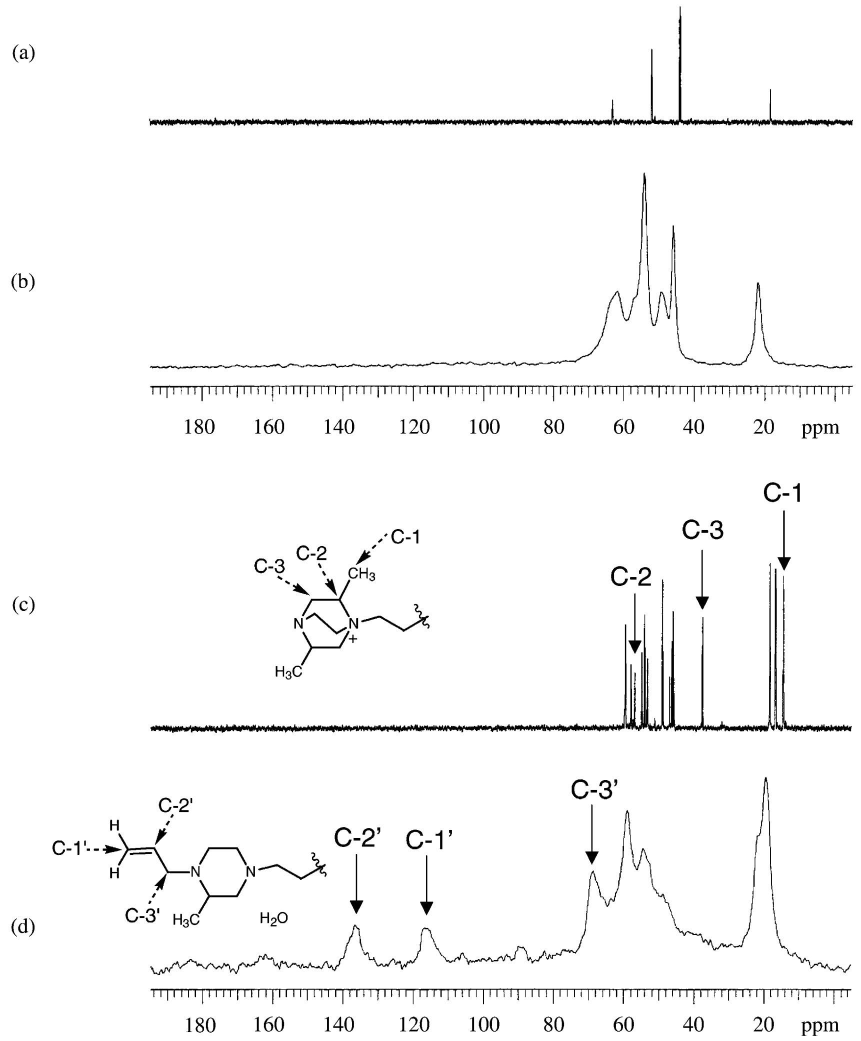


Fig. 3. ^{13}C NMR spectra of SDA and as-synthesized samples: (a) solution NMR of **1**; (b) CPMAS NMR of as-synthesized ZSM-12 obtained by using **1**; (c) solution NMR of **7**; (d) CPMAS NMR of as-synthesized GUS-1 obtained by using **7**.

of GUS-1 were extracted by full-profile fitting [27] using the GSAS software package [28] and normalized after estimation of the scale factor by a Wilson plot. The MOR-like structure found by model building was generated with the highest frequency among a variety of similar frameworks with 12-ring channels but different connectivity.

Distance least squares (DLSs) refinement [29] of the atomic positions gave a residual R-value R_{DLS} as low as $R_{\mathrm{DLS}} = 0.0029$ for space group *C222*, but a high value, $R_{\mathrm{DLS}} = 0.0150$, for space group *Cmmm* due to Si–O–Si bond angles of 180° imposed by symmetry.

The Rietveld refinement was performed in space group *C222* for GUS-1 and the space group *C2/c* was assumed for ZSM-12. The impurity SSZ-31 was ignored during the refinement. The final residuals of the Rietveld refinement are $R_{\mathrm{wp}} = 7.4\%$, $R_{\mathrm{p}} = 5.5\%$, and the R_{F} factors for the individual phases are $R_{\mathrm{F}} =$ 9.8 and 7.9% for GUS-1 and ZSM-12, respectively. The atomic positions of the calcined form of GUS-1 are shown in Table 4. The range of angles O–Si–O

Table 4
Fractional atomic coordinates for calcined GUS-1[a]

Atoms	*x*	*y*	*z*
Si1	0.3074 (17)	0.1879 (18)	0.478 (8)
Si2	0.1818 (21)	0.0767 (13)	0.527 (11)
Si3	0.0937 (16)	0.1222 (15)	0.016 (13)
Si4	0.0964 (17)	0.2819 (15)	−0.002 (14)
O1	0.3549 (30)	0.1874 (29)	0.754 (15)
O2	0.384 (4)	0.2092 (25)	0.307 (14)
O3	0.25	0.25	0.522 (24)
O4	0.2644 (26)	0.1170 (21)	0.477 (16)
O5	0.1537 (30)	0.0785 (24)	0.834 (11)
O6	0.212 (4)	0	0.5
O7	0.1151 (31)	0.1023 (21)	0.317 (13)
O8	0	0.1006 (35)	0
O9	0.1021 (18)	0.2021 (24)	−0.013 (11)
O10	0	0.297 (5)	0

[a] Crystal data: chemical formula $Si_{32}O_{64}$; space group *C*222; $a = 16.4206(4)$ Å; $b = 20.0540(4)$ Å; $c = 5.0464(1)$ Å; $V = 1661.8(1)$ Å^3.

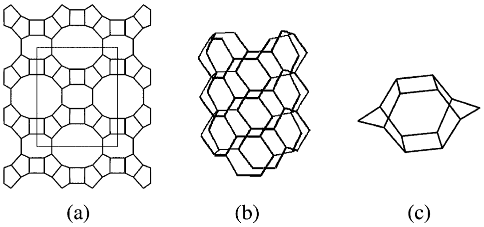


Fig. 4. The main structural features of GUS-1: (a) the [0 0 1] projection of GUS-1 is similar to that of mordenite (MOR); (b) the six-ring net channel; (c) the secondary building unit $4^25^46^2$ are common to that of ZSM-12 (MTW).

varied from 136 to 169°, and the length of Si–O has been maintained in the range 1.58–1.62 Å during the refinement.

GUS-1 was found to be a molecular sieve with one-dimensional 12-ring channels running along the *c*-axis. The channel aperture is elliptical in shape and the minor and major free diameters are 5.4 and 6.8 Å, respectively. The projection of the structure along the pores is very familiar, as it is the same as the projection of the well-known zeolite MOR in the *ab*-plane (Fig. 4a). On the other hand, GUS-1 shows many similarities with ZSM-12. Both structures possess the same channel net composed of six-rings only (Fig. 4b) and the same secondary building unit $4^25^46^2$ (Fig. 4c). In addition, the framework density of both structures are very close, FD = 19.3 T-atoms/nm^3. The framework

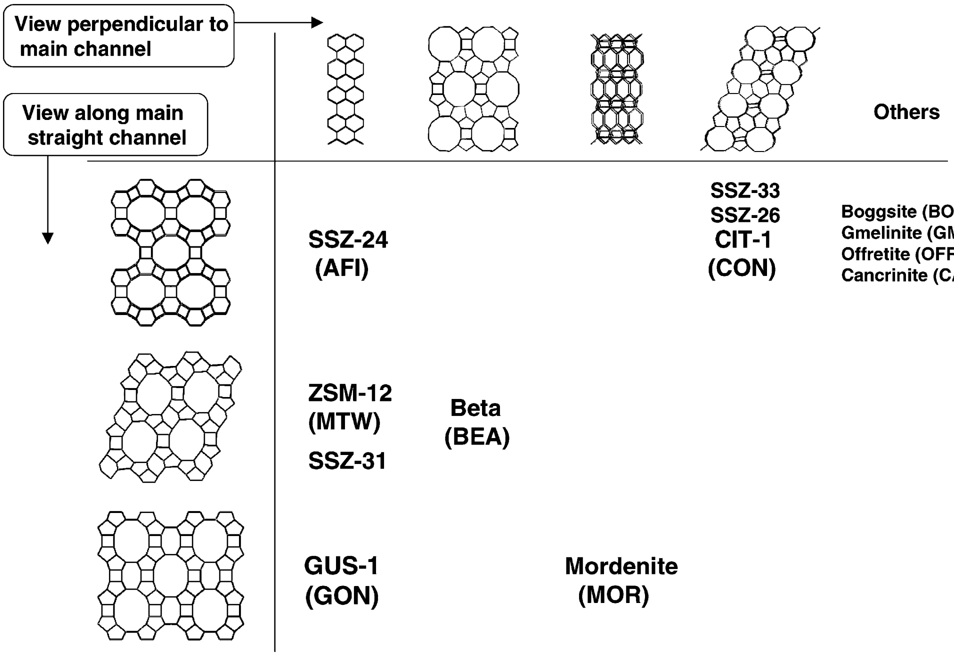


Fig. 5. Views along and perpendicular to the main straight channels of representative 12-ring molecular sieves.

type code of GUS-1 given by the Structure Commission of the International Zeolite Association is GON [21].

3.4. A structural feature of GUS-1

Fig. 5 illustrates representative molecular sieves having 12-ring straight channels. Views along the main straight channels as well as the views perpendicular to the main channels are given. Synthetic molecular sieves often have six-membered fused rings when viewed perpendicular to the main channels. The six-ring net has been one of the most common structural units. It is interesting to note that the phase having both MOR-type projection and six-ring net projection has long been unknown, and the GUS-1 is the first case as clearly seen in Fig. 5. The GUS-1 is considered to be “pure-silica MOR-analogue” or “MOR free of side-pore”.

4. Conclusions

DABCO derivatives **1**–**9** were designed and synthesized. When these cationic molecules were used as SDAs, ZSM-12, ZSM-5, or beta were obtained in most cases. Among them, the use of new cation **7** gave a novel crystalline phase that was designated GUS-1. Pure-silica conditions were particularly preferable for the synthesis of GUS-1. GUS-1 had high stability to heat as well as large adsorption capacity. The GUS-1 was indexed in the orthorhombic crystal class with refined lattice constants $a = 16.4206(4)$ Å, $b = 20.0540(4)$ Å, and $c = 5.0464(1)$ Å. The crystalline architecture of GUS-1 showed common features to both MOR and ZSM-12. The projection of the framework along the pore was similar to the projection of MOR in the *ab*-plane; the channel net and the secondary building unit of GUS-1 were closely related to that of MTW.

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