GUS-1: a mordenite-like molecular sieve with the 12-ring channel of ZSM-12†

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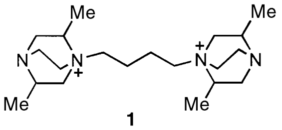
The framework topology of the novel molecular sieve GUS-1 is reported; the crystalline architecture is characterized by a one-dimensional 12-membered ring channel system that is closely related to the channels of mordenite and ZSM-12.

The search for new microporous solids has shown some successes in recent years as the number of new topologies has doubled within a decade.[1] A key factor is the use of the structure-directing effects of organic species for generating new frameworks. We report here the structure of a novel molecular sieve GUS-1 using 1,1′-butylenedi(4-aza-1-azonia-2,5-dimethylbicyclo[2.2.2]octane) dihydroxide (**1**-hydroxide) as organic structure-directing agent (SDA).

The GUS-1-containing sample was synthesized under hydrothermal conditions. A synthesis mixture of composition $1SiO_2:0.1R^{2+}(OH^-)_2:0.1NaOH:50H_2O$, where the silica source was fumed silica (Cab-O-Sil M-5, Cabot), was heated at 150–175 °C statically under autogeneous pressure for 10–20 d. In order to remove the occluded organics, the sample was calcined at 700 °C for 6 h in air. R^{2+} stands for structure **1** and its hydroxide form, **1**-hydroxide, was prepared by refluxing 1,4-dibromobutane and excess 2,5-dimethyl-1,4-diazabicyclo[2.2.2]octane in acetone–methanol, followed by ion-exchange.§



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The GUS-1 phase tends to come along with ZSM-12, and the synthesis of the new phase in pure form has not been successful so far. Synthesis under all-silica conditions gave a sample with relatively higher GUS-1 content, making structure elucidation of the new phase possible. Further synthetic details are forthcoming.

Structure determination of GUS-1 was carried out from synchrotron powder diffraction data. The powder pattern was collected at the X7A beamline at the National Synchrotron Light Source at Brookhaven Laboratory. The calcined sample was packed in a 1 mm capillary. Acquisition was carried out at room temperature at the wavelength $\lambda = 1.196417$ Å.

The reflections of GUS-1 were indexed using the program TREOR.[2] A solution was obtained in the orthorhombic system with lattice constants $a = 16.411(2)$, $b = 20.044(2)$, $c = 5.0427(3)$ Å and figures of merit[3,4] $M(16) = 53$ and $F(16) = 60(0.003,85)$, after refinement of the unit-cell. Systematic absences indicate C-centering and are consistent with the space groups *Cmmm* and subgroups, and possibly $C222_1$.

A weak, unindexed line is found at position $d = 14.4$ Å. The interplanar distance is characteristic of the (100) reflection of zeolite SSZ-31.[5] The other peaks of SSZ-31 are not visible in the powder pattern due to the high density of peaks and the structural relations between SSZ-31 and ZSM-12. The SEM pictures show a large number of particles with the typical needle shape of ZSM-12 crystals. Overgrowth of thin needles is observed on the crystallites of ZSM-12, which is assigned to GUS-1. A small number of particles with the fan-like morphology characteristic of SSZ-31 crystallites are also present in the sample.[5]

GUS-1 possesses a small *c*-axis, $c = 5.0$ Å, reducing the structure determination to a search of the two-dimensional projection of the zeolite into the *ab* plane of the cell. In addition, the N_2 adsorption measurements reveal that the adsorption isotherm of the sample containing the two phases, GUS-1 and ZSM-12, is very similar to the isotherm of pure ZSM-12, suggesting that the unknown phase is a molecular sieve with 12-ring channels too. Models have been built with *Cmmm* symmetry and 12-ring channels running along the *c*-axis. A good candidate was found showing the same projection as mordenite along the pore. The model contains four independent tetrahedral sites of equal multiplicity, in agreement with the ^{29}Si MAS NMR spectrum of the sample where three lines in the ratio 1:2:1 are observed in addition to the seven peaks of ZSM-12.[6]

An optimization of the geometry of the framework has been performed using a distance least squares (DLS)[7] refinement of the atomic positions in space group *Cmmm* and subgroups, assuming a distance $d_{Si–O} = 1.61$ Å. The model refined in space group *Cmmm* shows a high residual *R* value, R_{DLS} 0.0150. However, typical R_{DLS} values are obtained for the subgroups *Cmm*2 and *C*222 where $R_{DLS} = 0.0024$ and 0.0029, respectively. A high R_{DLS} value indicates strong distortions of the framework in the presence of a reflection plane in the *ab* plane. The framework with *Cmmm* symmetry exhibits Si–O–Si bond angles of 180° due to the presence of a bridging oxygen atom on an inversion center. Straight Si–O–Si bond angles are recurrent in the mordenite group, as an oxygen atom is found on an identical symmetry element in mordenite[8] and dachiardite.[9] The 180° bond angle constraint is released by reducing the symmetry of the framework to *Cmm*2 or *C*222.

Further framework searches were performed using the program FOCUS.[10,11] The structure factors of the phase GUS-1 were extracted using the Lebail method[12] in the GSAS software[13] and normalized after estimation of the scale factor by a Wilson plot.

The mordenite-like structure found by model building was generated with the highest frequency. A variety of frameworks with 12-ring channels was also obtained. Most of them are derived from the same mordenite sheet but distorted with the bonds directed up or down at different nodes. All these solutions were discarded based on the poor match of their simulated powder pattern to the experimental data and the high R_{DLS} values.

The Rietveld refinement was performed with the two phases in approximate composition 40% GUS-1 and 60% ZSM-12. The impurity SSZ-31 was ignored during the refinement. The space group *C*222 was selected for the framework of GUS-1 and

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† Electronic supplementary information (ESI) available: details of the synthesis of the SDA, crystal data and fractional atomic coordinates for GUS-1. See http://www.rsc.org/suppdata/cc/b0/b005225f/

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the initial atomic coordinates were the positions obtained from the DLS refinement. For ZSM-12 the powder pattern shows the superstructure reflections indicating the doubling of the *c* dimension. The space group is assumed *C*2/*c* and the atomic positions obtained by Fyfe *et al.* were used as starting model.[6] Peak broadening corrections due to particle size effects were applied for both phases. Soft geometric constraints on the Si–O distances were maintained for the two structures until the final stage of the refinement.

Fig. 1 shows a close fit between the calculated and the experimental powder pattern confirming the framework topology of GUS-1. The final residuals are R_{wp} = 7.4%, R_p = 5.5%, and the R_F factors for the individual phases are R_F = 9.8 and R_F = 7.9% for GUS-1 and ZSM-12 respectively.¶

The Si–O distances were maintained for both structures in the range 1.58–1.62 Å. For GUS-1 the averaged Si–O distance $d_{\text{Si–O}}$, is 1.60 Å and the Si–O–Si bond angles range from 136 to 169° with an average of 151°.

The Rietveld refinement performed for the space group *Cmm*2 for GUS-1 gave slightly higher *R* factors. The coexistence in the sample of two other phases (including the SSZ-31 impurity) probably introduces a bias in the structure refinement of GUS-1 as the line intensities cannot be properly estimated. It should be noted in particular that the Si–O distances reported by Fyfe *et al.* for the refinement from synchrotron data of all-silica ZSM-12 vary from 1.53–1.70 Å, suggesting that the structure model adopted for ZSM-12 is not completely satisfactory.[6] Therefore, the main result of the Rietveld refinement with the available data is the confirmation of the framework topology of GUS-1.

The structure of GUS-1 is shown in Fig. 2. GUS-1 is a molecular sieve with one-dimensional, 12-ring channels running along the *c*-axis. The projection of the structure in the *ab* plane is similar to the projection of mordenite along the pores [Fig. 2(a)]. GUS-1 shows also common features with ZSM-12. Both structures have the same framework density, *TD* = 19.3 Si atoms per nm^3, have a short axis with a repeat unit of *ca.* 5 Å and possess the same secondary building unit $4^25^46^2$ [Fig. 2(b)]. But the most striking similarity is the channel structure: both zeolites have an identical channel net composed of six-rings only [Fig. 2(c)]. The channel aperture of GUS-1 is elliptical in shape with deformation from circular shape intermediate between mordenite and ZSM-12. The minor and major free diameters are 5.6 and 7.0 Å, respectively, calculated in the topological symmetry *Cmmm*, with an oxygen radius 1.35 Å.[1]

It is worth mentioning that linear faults along the pore direction have been found in mordenite.[14–16] Different strain-free structures related to mordenite can be obtained by half unit-cell shifts of the four-ring columns along the *c*-axis.[17,18] A simple model describes the faulting as a one-half shift of the *c*-axis,[14,16] which leads to the formation of units $4^25^46^2$ [Fig. 2(b)]. The framework of mordenite can adopt locally the GUS-1 topology in a highly defective sample by gathering of faults.

In summary, the crystal structure of a new high-silica microporous solid has been elucidated from the synchrotron powder X-ray diffraction data of a mixture of phases. The new framework GUS-1 has symmetrical topology *Cmmm* and shows structural relationships with both mordenite and ZSM-12 frameworks. The formation of ZSM-12 in the presence of GUS-1 may be partly due to the instability of the present SDA.‖ The search for a new SDA that is more stable and suitable for GUS-1 formation is now in progress.

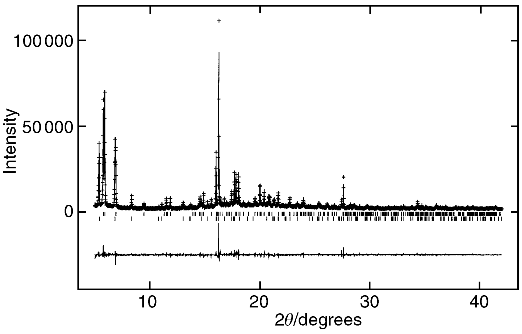

Fig. 1 Observed and calculated synchrotron powder X-ray diffraction pattern of the calcined mixture 40% GUS-1 and 60% ZSM-12 (λ = 1.196417 Å). The upper vertical bars correspond to the peak positions of ZSM-12 and the lower bars represent the peak positions for GUS-1.

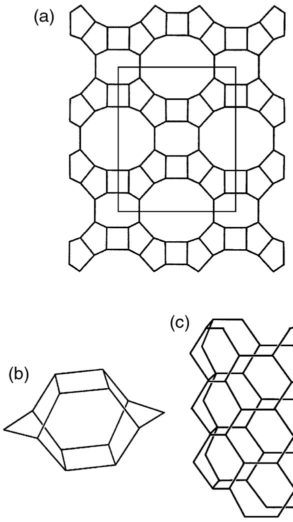

Fig. 2 Structure of GUS-1. (a) projection of the GUS-1 net onto the *ab* plane, (b) the secondary building unit $4^25^46^2$ and (c) the six-ring net channel.

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Notes and references

§ The SDA **1** in both bromide and hydroxide forms gave reasonable ^{1}H and ^{13}C NMR spectra. On a spectroscopic basis, the purity of the SDA was $\geqslant$90% just before use.

¶ CCDC 182/1782. See http://www.rsc.org/suppdata/cc/b0/b005225f/ for crystallographic data in .cif format.

‖ Obvious formation of an allylpiperazine moiety was observed in the ^{13}C CP MAS NMR spectrum of the as-synthesized sample, indicating that some partial decomposition *via* the Hofmann elimination had occurred.

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