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Synthesis of microporous gallosilicates with the CGS topology†

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Zeolite TNU-1 (Taejon National University Number 1), a gallosilicate possesing the CGS topology with a three dimensional system of medium and small pores, crystallises in the presence of Ga in conditions in which the presence of Al yields merlinoite-type zeolites.

A wealth of zeolite structures[1] have been synthesised during the last 30 years through the use of organic additives which are commonly known as structure-directing agents (SDAs). These SDA additives are believed to 'select' between different possible zeolite structures.[2] The precise mechanism of the structure direction by organic additives is not well understood, but since they generally end up occluded within the void spaces of the crystallised zeolite, it is thought that the size and shape of the SDA may determine to some extent the size and shape of those void spaces. This 'second generation' of zeolites is typically characterised by a moderate to very high Si/Al ratio as opposed to the first generation of synthetic zeolites (those prepared mainly in the 1950s, 1960s and 1970s without the use of organic additives and possessing Si/Al ratios generally below 5).

On the other hand, recent reports have suggested heteroatoms (*i.e.*, an atom different from Si which may be incorporated in tetrahedral positions) can exert some structure-directing influence over the crystallisation of zeolite-like materials. Probably, the clearest case in this respect is Zn^{2+} (and Be^{2+}) since in its presence microporous solids with topologies tantalisingly different from those of aluminosilicate zeolites are able to crystallise.[3] This has been rationalised through the definite preference for Zn^{2+} (and Be^{2+}) to occupy tetrahedral positions with very narrow T–O–T angles, which is in turn a consequence of the low ratio of non-bonded radius to T–O distance for these heteroatoms.[4] The striking case of the large pore VPI-8 zincosilicate, which only nucleates in the presence of Zn^{2+}, is paradigmatic since the structure-directing ability of Zn^{2+} largely surpasses that of several organic additives that can also be used in the synthesis.[5] A completely different case appeared to be that of Ga^{3+}, which has been extensively used, sometimes in combination with organic additives, to produce materials isostructural to known aluminosilicate zeolites.[6] Up till now, however, no new silicate-type zeolite structures have been produced as a result of the presence of Ga^{3+} in the synthesis mixture. We report here the synthesis and structure of a low-silica zeolite-like material denoted TNU-1,[7] having no counterpart amongst aluminosilicates, and one that reveals how Ga^{3+} can also play a structure-directing role in the synthesis of microporous materials. TNU-1 is isostructural to the MGaPO-6 ($M = Co^{II}$, Zn^{II}) materials, whose structure was very recently reported[8] and assigned the structure code CGS.[9]

In a typical synthesis TNU-1 was synthesised as follows: 1.87 g of gallium oxide (Aldrich), 14.96 g of KOH (45% aqueous solution, Aldrich), and 8.69 g of deionised water were mixed in a plastic vessel and heated overnight at 100 °C. To this translucent solution 15.0 g of colloidal silica (Ludox AS-40, DuPont) was added (final composition: 6.0 K_2O : 1.0 Ga_2O_3 : 10.0 SiO_2 : 150 H_2O). After stirring at room temperature for 1 day, the resultant reaction mixture was crystallised in a Teflon-lined autoclave at 150 °C for 10 days. The recovered solid has the composition 1.0 K_2O : 1.0 Ga_2O : 4.2 SiO_2 : 2.2 H_2O. A summary of the synthetic results under different conditions but using the synthesis procedure described above is presented in Table 1.

Under the conditions reported, two gallosilicate materials were obtained depending on the nature and relative amount of the alkali metal cations (Table 1). TNU-1 was obtained in the presence of K or mixtures of Na and K with $K/Na > 1$. When the Na content was increased above $Na/K = 1$ a gallosilicate with the NAT topology was obtained. The strong influence of the alkali cation on the crystallization product is not unexpected, since similar observations are common in aluminosilicate zeolite synthesis in the absence of organic additives.[10] Of particular interest is the observation that when gallium oxide is replaced by the equivalent amount of $Al(OH)_3$ under the conditions described above, a merlinoite-type zeolite was obtained. This clearly shows that the presence of Ga in the reaction mixture is a critical factor directing the crystallisation of TNU-1. Even when triethylamine or tetraethylammonium hydroxide are added to the synthesis mixture TNU-1 is the phase that crystallises in the presence of Ga (Table 1), revealing that its structure-directing ability is robust enough to surpass any directing role from the organic additives (*N.B.* these are not occluded in the zeolite). By contrast, crystallization of the aluminosilicate CGS analog was not possible even in the

Table 1 Representative synthesis conditions and results[a]

K_2O	Na_2O	R[b]	T/°C	t/days	Product
6.0	0.0	0	150	10	Gallosilicate TNU-1 (CGS)
6.0	0.0	0	150[c]	7	Aluminosilicate MER
6.0	0.0	0	150[c,d]	7	Aluminosilicate MER
4.8	1.2	0	150	10	Gallosilicate TNU-1 (CGS)
3.6	2.4	0	150	10	Gallosilicate TNU-1 (CGS)
2.4	3.6	0	150	10	Gallosilicate NAT
1.2	4.8	0	150	10	Gallosilicate NAT
0	6.0	0	150	10	Gallosilicate NAT
4.8	0	2.4	150	5	Gallosilicate TNU-1 (CGS)

[a] Composition of the synthesis mixture (unless otherwise stated): 6.0 M_2O : 1.0 Ga_2O_3 : 10 SiO_2 : 150 H_2O, where M is K+Na+R. [b] R = tetraethylammonium hydroxide or triethylamine. [c] Ga replaced by Al in the above composition. [d] 1% TNU-1 crystals added as seeds.

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†Electronic Supplementary Information (ESI): Rietveld X-ray powder diffraction of TNU: 1. Crystallographic data, atomic parameters, framework distances and angles and isotropic thermal parameters. See http://www.rsc.org/suppdata/jm/1999/2287

presence of TNU-1 seeds: the synthesis in the presence of 1% TNU-1 crystallites again yielded MER.

Typical synthesis of TNU-1 produced highly crystalline samples yielding a well resolved powder XRD pattern. This pattern could be indexed on an orthorhombic unit cell ($a = 8.66$, $b = 14.17$, $c = 16.33$ Å) having systematic absence conditions consistent with space groups *Pnma* and $Pn2_1a$. Despite the relatively large number of independent atoms (13 framework plus 8 extraframework) the framework structure was solved in *Pnma* from synchrotron diffraction data by direct methods (Sirpow)[11] from LeBail extracted intensities.[12] The extraframework atoms were located in Fourier maps during full Rietveld refinement of the structure (GSAS).[13] It was clear from the start that K and H_2O within the channels present some disorder and the final model represents a tentative interpretation of the residual electron density after inclusion of the framework atoms. In the latter stages of the refinement attempts were made to refine Ga/Si occupancies but no evidence for Ga/Si ordering was observed. Details on data collection, crystallographic information, Rietveld plots and selected bond distances and angles information have been deposited as supplementary materials (ESI).

After the crystal structure was solved it was realised that it shares the same framework topology as Me-GaPO-6 (Me = Co/Zn), IZA code CGS. Furthermore, a very recent report concerning the single crystal structure determination of TsG-1[14] reveals this material similarly possesses the same framework topology. The structure itself comprises a system of 10MR–8MR–8MR channels giving rise to a rather open structure. Fig. 1 shows the 10MR channel along [100] and the 8MR channel along [010]. The second 8MR channel lies along [011] and is sinusoidal in character, having the 8MR windows offset from one to the next. The topology of TNU-1 is coincident with that of Me-GaPO-6 materials.

The ^{29}Si MAS NMR spectrum of TNU-1 is shown in Fig. 2 together with a deconvolution of the spectrum and the assignment to $Si(OGa)_n(OSi)_{(4-n)}$ species. The assignment is based on the known range of chemical shifts for gallosilicate zeolites having similar Si/Ga ratios.[15] We find a splitting of resonances for species with the same *n*, as observed also in other gallosilicate zeolites. For TNU-1, this may be related to the relatively small T–O–T angle for site T1 (135.8°). Based on the assignment in Fig. 2 and assuming avoidance of Ga–O–Ga linkages the Si/Ga ratio derived from the intensities of the deconvoluted components of 1.9 is found to be very close to the experimental value of 2.1. The relative intensities of species with values of *n* from 4 to 0 are 6.6, 26.2, 40.1, 22.3 and 4.7%, respectively, which is reasonably close to that expected assuming an even distribution of Ga and Si over the available tetrahedral sites for a Si/Ga ratio of 1.9 with avoidance of Ga–O–Ga linkages (5.4, 23.2, 37.4, 26.8 and 7.2%). This result agrees with our structure refinement of TNU-1 from high resolution powder diffraction data, which gave no indication of Si/Ga ordering over the tetrahedral sites of the CGS topology. We note that the single crystal investigation of TsG-1 gave the same result.

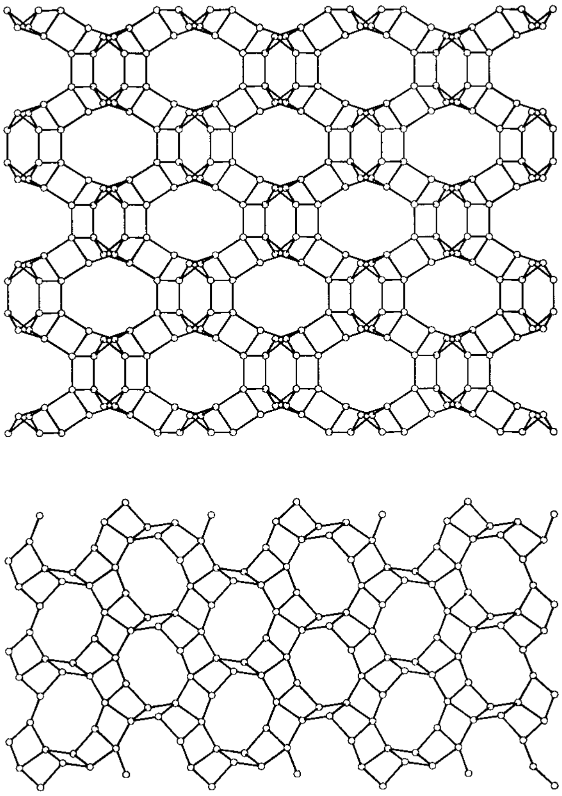

Fig. 1 The structure of TNU-1 in projection along [100] (top) and along [010] (bottom) showing the linear 10MR and 8MR channels, respectively. Only the tetrahedral connectivity is represented.

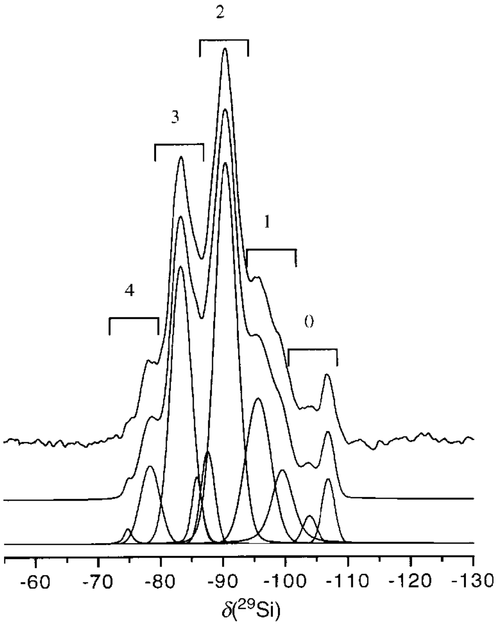

Fig. 2 ^{29}Si MAS NMR spectrum of TNU-1: experimental (top), simulated (middle) and deconvoluted components (bottom). The assignment to $Si(OGa)_n(OSi)_{(4-n)}$ species is also given.

Since Ga and Si are evenly distributed in TNU-1 the structure-directing ability of Ga appears to be different from that of either Be or Zn mentioned above, where structural and NMR characterization showed a strong tendency to order. This is not unexpected, since the ratio of non-bonded radius to T–O distance for Ga (NBR/TO = 0.88) is closer to that of Si (0.93) than those of Be^{2+} (0.82) or Zn^{2+} (0.83). Notwithstanding this, the relatively low NBR/TO ratio of Ga compared to Si could possibly favour the formation of structures with low T–O–T angles, similarly, but in a less stringent way to Zn and Be. Actually, Newsam and Vaugham[16] observed a general decrease of the T–O–T angles in a number of gallosilicate zeolite structures determined by neutron diffraction when compared to their aluminosilicate analogs, and wondered if the tendency of Ga towards relatively small T–O–T angles could eventually lead to excessive constraints on certain zeolite topologies prohibiting the formation of their gallosilicate analogs. This could be a way of structure direction by Ga, explaining why MER is not formed when Al is replaced by Ga under the synthesis conditions reported here. As a matter of fact, aluminosilicate MER materials have a slightly larger average T–O–T angle (140.9°) than gallosilicate CGS materials (139.1° found in this work or 135.7° derived from single crystal diffraction), but the differences are small. The mechanism of structure direction by Ga remains however puzzling and we are currently trying to ascertain what other conditions are needed for Ga to produce new structures rather than analogs of already known aluminosilicate materials. Nevertheless, TNU-1 does indeed reveal that novel gallosilicate structures can be produced, which in our view yields a viable alternative route to the discovery of novel low-silica zeolite-like materials.

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