TNU-7: A Large-Pore Gallosilicate Zeolite Constructed of Strictly Alternating MOR and MAZ Layers

Stewart J. Warrender,[†] Paul A. Wright,[†] Wuzong Zhou,[†] Philip Lightfoot,[†] Miguel A. Camblor,[‡] Chae-Ho Shin,[§] Dong Ja Kim,[||] and Suk Bong Hong*,[||]

School of Chemistry, University of St. Andrews, St. Andrews KY16 9ST, U.K., Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Campus Cantoblanco, 28049 Madrid, Spain, Department of Chemical Engineering, Chungbuk National University, Chungbuk 361-763, Korea, and Division of Chemical Engineering, Hanbat National University, Taejon 305-719, Korea

Received December 22, 2004
Revised Manuscript Received February 5, 2005

Zeolites and related microporous solids find widespread application in many technologies, including ion exchange, separation, and catalysis. Their advantages over other solids stem directly from their high surface areas and structure-dependent pore geometries and cation environments. As a consequence, considerable effort is expended in the design of new zeolitic materials with structural features that could lead to improvement or development of commercial processes. While many novel zeolite structures have been discovered through the use of inorganic and/or organic additives, commonly known as structure-directing agents (SDAs), recent advances in this research area have shown that the introduction of heteroatoms such as Li, Be, B, Zn, and Ge into silica frameworks during the crystallization process is another effective way to obtain novel topologies.[1] This also appears to be the case for Ga, the element most similar to Al, despite the general notion that the gallosilicate product is the same as for the aluminosilicate crystallization.[2] Our investigations into the structure-directing effect of Ga in zeolite syntheses have revealed that replacement of Al by Ga at low-silica compositions can give microporous materials with topologies different from those of aluminosilicate zeolites prepared under otherwise identical conditions.[3] The synthesis of the gallosilicate TNU-1 (framework type CGS) is an example for which no counterpart has been reported among aluminosilicate zeolites. This material, which had two precedents denoted as TsG-1 and ECR-9 in the literature,[4] comprises a three-dimensional pore system with intersecting 10- and 8-ring channels.[3a] ECR-34 (ETR), the first gallosilicate zeolite having 18-ring pores,[5] the crystallization of which requires the combined use of Na^+, K^+, and tetraethylammonium ions as SDAs, is another example.

On the other hand, many zeolite structures are composed of a single type of complex silicate layer, joined to adjacent layers by T−O−T bonds that are approximately perpendicular to the plane of the layers. Hence, there are very few structures that can be regarded as being derived by the stacking of more than one different type of layer with coincident arrangements of T−O groups as possible points of attachment. One example of the latter case is zeolite ECR-1, first synthesized by Vaughan and Strohmaier in the presence of a rather sophisticated organic cation, bis-(2-hydroxyethyl)dimethylammonium.[6a] ECR-1 has been proposed to consist of structural layers of mordenite (MOR) and mazzite (MAZ) connected in a regular 1:1 stacking sequence.[6b] Due to the very thin (<0.1 μm) nature of its crystals and the presence of stacking faults, however, the powder XRD patterns of ECR-1 display relatively broad lines. Thus, no structure refinement of this zeolite has been possible. Here we present the structure solution of TNU-7 (Taejon National University number 7), a large-pore gallosilicate zeolite constructed of ordered, alternating layers of the MOR and MAZ structures, which is one of a series of microporous gallosilicates recently prepared in our laboratory in the absence of organic SDAs.[3]

Microporous materials were crystallized under hydrothermal conditions (45-mL PTFE-lined stainless steel autoclaves (degree of filling ca. 60%), 150 °C, rotation (60 rpm), 7 days, composition: $2.0Na_2O{\cdot}xM_2O_3{\cdot}10.0SiO_2{\cdot}150H_2O$, where M is Al or Ga and x is varied between $0.125 \le x \le 2.0$). Gallium oxide (99.99+%, Aldrich) or aluminum hydroxide ($Al(OH)_3{\cdot}0.5H_2O$, Strem) was first mixed with a solution of NaOH (50% aqueous solution, Aldrich) in water and then heated overnight at 100 °C. To the resulting clear solution, after cooling to room temperature, colloidal silica (Ludox AS-40, DuPont) was added and stirred for 1 day, prior to heating at 150 °C. Table 1 summarizes the synthesis results and shows that the crystallization of TNU-7 depends critically on the presence of Ga in the synthesis mixture, as well as on its content. Variation of the Ga concentration results in the sequential formation of gallosilicate analcime (ANA), mazzite, TNU-7, and mordenite as the Ga concentration decreases, whereas substitution of Ga by Al results in the

* To whom correspondence should be addressed. Tel: +82-42-821-1549. Fax: +82-42-821-1593. E-mail: sbhong@hanbat.ac.kr.
[†] University of St. Andrews.
[‡] Consejo Superior de Investigaciones Científicas.
[§] Chungbuk National University.
[||] Hanbat National University.

(1) International Zeolite Association, Structure Commission. http://www.iza-structure.org.
(2) Fricke, R.; Kosslick, H.; Lischke, G.; Richter, M. *Chem. Rev.* **2000**, *100*, 2303.
(3) (a) Hong, S. B.; Kim, S. H.; Kim, Y. G.; Kim, Y. C.; Barrett, P. A.; Camblor, M. A. *J. Mater. Chem.* **1999**, *9*, 2287. (b) Cho, H. H.; Kim, S. H.; Kim, Y. G.; Kim, Y. C.; Koller, H.; Camblor, M. A.; Hong, S. B. *Chem. Mater.* **2000**, *12*, 2292. (c) Kim, S. H.; Kim, S. D.; Kim, Y. C.; Kim, C.-S.; Hong, S. B. *Micorporous Mesoporous Mater.* **2001**, *42*, 121. (d) Paik, W. C.; Camblor, M. A.; Hong, S. B. *Stud. Surf. Sci. Catal.* **2001**, *135*, [CD-ROM] Paper 05-P-07. (e) Hong, S. B.; Lee, S.-H.; Shin, C.-H.; Woo, A. J.; Alvarez, L. J.; Zicovich-Wilson, C. M.; Camblor, M. A. *J. Am. Chem. Soc.* **2004**, *126*, 13742.
(4) (a) Krutskaya, T. M.; Kolishev, A. N.; Morozkova, V. E.; Berger, A. S. *Zh. Neorg. Khim.* **1985**, *3*, 783. (b) Vaughan, D. E. W.; Strohmaier, K. G. U.S. Patent 5,096,686, 1992.
(5) Strohmaier, K. G.; Vaughan, D. E. W. *J. Am. Chem. Soc.* **2003**, *125*, 16035.
(6) (a) Vaughan, D. E. W.; Strohmaier, K. G. U.S. Patent 4,657,748,-1987. (b) Leonowicz, M. E.; Vaughan, D. E. W. *Nature* **1987**, *329*, 819. (c) Chen, C. S. H.; Schlenker, J. L.; Wentzek, S. E. *Zeolites* **1996**, *17*, 393.

10.1021/cm0477467 CCC: $30.25
Published on Web 02/25/2005

Table 1. Syntheses from Gel Composition $2.0Na_2O{\cdot}xMe_2O_3{\cdot}10SiO_2{\cdot}150H_2O$[a]

Si/Me ratio in the gel	product[b,c]	
	Me = Ga	Me = Al
2.5	analcime (2.52)	amorphous
3.0	analcime + mazzite	amorphous[e]
3.0[d]	mazzite (3.03)	amorphous[e]
4.0	mazzite + TNU-7	*f*
5.0	TNU-7 (3.85)	mordenite (4.56)
7.5	mordenite	mordenite
10	mordenite (5.89)	mordenite (9.61)
20	mordenite + (kenyaite)	mordenite
40	kenyaite + (mordenite)	*f*

[a] x is varied between $0.125 \leq x \leq 2.0$. Crystallization was performed under rotation (60 rpm) at 150 °C for 7 days, unless otherwise stated. [b] The phase appearing first is the major phase, and the product obtained in a trace amount is given in parentheses. [c] The values given in parentheses are Si/Ga or Si/Al ratios of the product, as determined by elemental analysis.[d] A small amount (2 wt % of silica in the synthesis mixture) of the calcined gallosilicate with Si/Ga = 2.60 or aluminosilicate mazzite with Si/Al = 3.17 prepared in the presence of tetramethylammonium ion[7] was added as seeds prior to heating at 150 °C for 3 days. [e] After heating at 150 °C for 14 days. [f] Not performed.

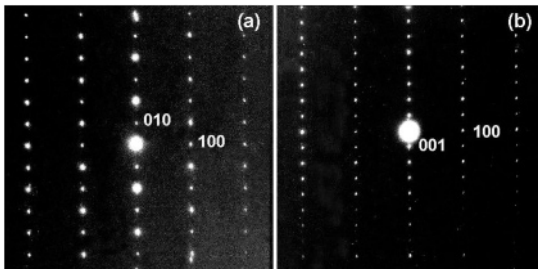

Figure 1. SAED patterns of TNU-7 along (a) the [001] zone axis and (b) the [010] zone axis (JEOL 2011 transmission electron microscope operating at 200-kV accelerating voltage).

crystallization of mordenite at intermediate and low Al contents.

A combination of elemental and thermal analyses indicates, within experimental error, that TNU-7 has the chemical composition $Na_{12.4}Ga_{12.4}Si_{47.6}O_{120}{\cdot}30.9H_2O$ (based on the unit cell of the as-made material, see below). Its powder XRD pattern can be indexed as orthorhombic, with $a = 7.59$, $b = 18.01$, and $c = 26.08$ Å, and shows systematic absences consistent with space group *Pmmn*. The unit cell dimensions and symmetry of TNU-7 match well with the two models ECR-1A and ECR-1B proposed by Leonowicz and Vaughan[6b] for aluminosilicate ECR-1 and investigated by Chen et al.[6c] These two models differ in the connectivity of their alternating MOR and MAZ layers: in ECR-1A, the layers are connected by chains of 5-rings, whereas in ECR-1B they are connected via chains of alternating 4- and 6-rings. The selected area electron diffraction (SAED) patterns of TNU-7 are given in Figure 1. The pattern in Figure 1b, taken along the [010] zone direction, shows no detectable streaking, clearly indicating that the layers in TNU-7 are stacked in a strictly alternating fashion, unlike those in ECR-1, which exhibits extensive stacking disorder.[6]

When the XRD pattern of TNU-7 is compared with the calculated patterns for both models, it is evident that model ECR-1A is preferred for TNU-7, as suggested by Chen et al. for ECR-1.[6c] For the Rietveld refinement, therefore, the framework atomic coordinates reported for ECR-1A were taken as a starting model (details of the refinement are given in the Supporting Information). The final refined structure of TNU-7 with Na^+ ion locations is shown in Figure 2. The material possesses a three-dimensional pore system in which layers of MOR and MAZ structures are linked in a strictly alternating manner via chains of 5-rings, which run parallel to *a*. As a consequence of the strict alternation of MAZ and MOR sheets, the main 12-ring channels (6.6×7.4 Å), which also parallel *a*, are asymmetric (Figure 3). Access from the main channel to the interchannel regions is only possible through the MOR layers via slightly distorted 8-rings into the MAZ sheet, as seen in Supporting Information. Movement along *b* is only possible along the MAZ sheets. The distribution of Na^+ ions is also asymmetric (Figure 2). Na^+ ions are located within the 12-ring channel near the MAZ layers and within 8-ring windows adjacent to the MOR

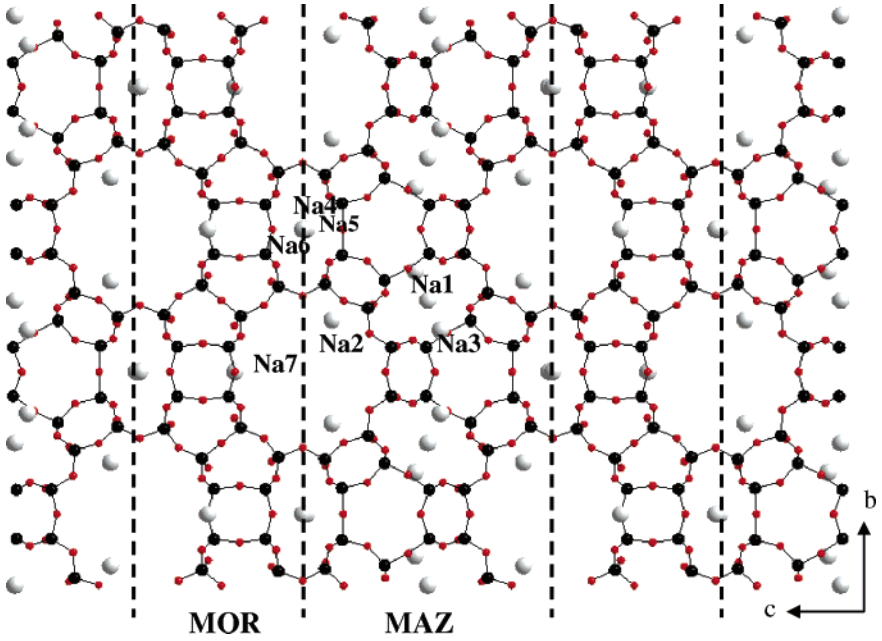

Figure 2. Refined structure of TNU-7 with refined Na^+ ion locations, viewed along [100].

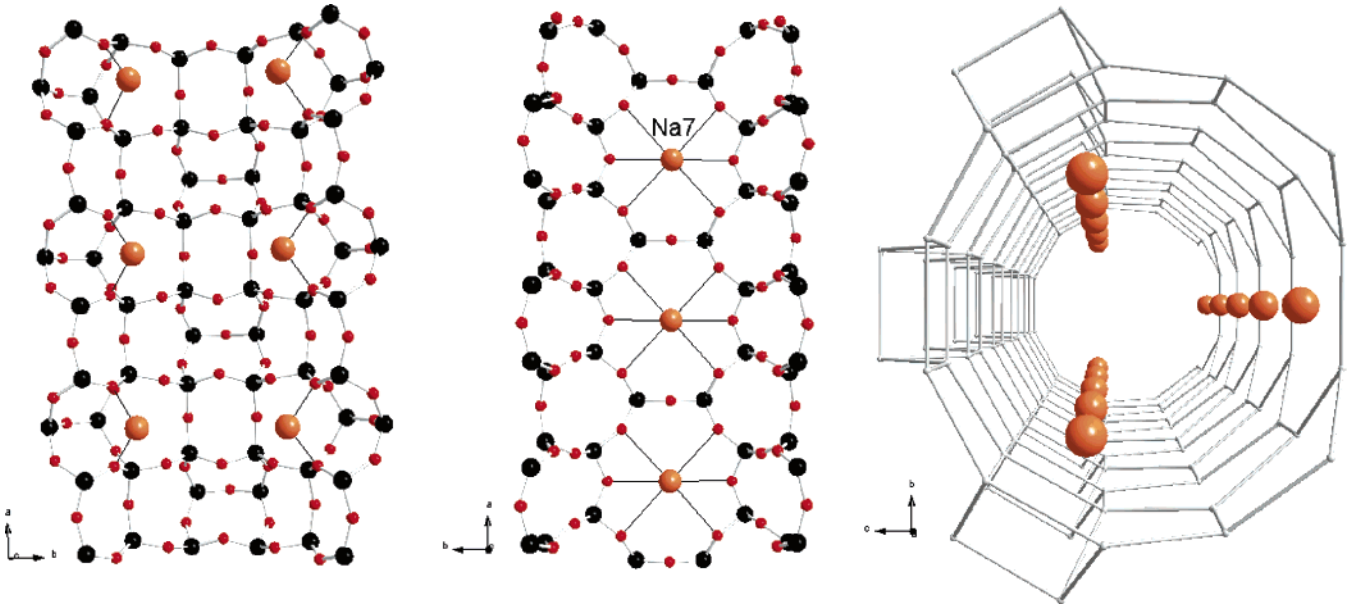

Figure 3. Cut-away diagram of the main channel viewed (a) along $+c$ and (b) along $-c$; (c) main channel viewed along *a* (oxygens removed for clarity).

layers. Zigzag chains of Na^+ ions (Na(1) and Na(3)), running parallel to *a*, have been located within the MAZ sheets (analogous to Na-MAZ itself) and a nearly linear chain of Na^+ ions (Na(4), Na(5), and Na(6)) is located in the smaller of the inter-sheet channels. The physicochemical properties of TNU-7 and further details of its synthesis and structure will be given elsewhere.

In conclusion, we have determined and refined the structure of TNU-7, a large-pore gallosilicate zeolite in which MOR and MAZ sheets are connected via chains of 5-rings in a strictly ordered, alternating manner. The lack of stacking disorder allowed the refinement of the structure, confirming model ECR-1A as a new zeolite topology. The crystallization of TNU-7 in conditions surrounded by the crystallization fields of the structurally related MAZ and MOR may encourage the use of the boundary phase strategy proposed by Vaughan[5,6b,8] for the discovery of novel "designer" structures. As shown in this work, this strategy can be used in combination with the structure-direction effect of Ga without recourse to organic SDAs.

Acknowledgment. This work was partially supported by KOSEF (R02-2003-000-10087-0 to S.B.H.).

Supporting Information Available: Details of the structure refinement, final atomic coordinates, selected bond distances and angles, final Rietveld plot, and diffusion pathways in the *ab* plane (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM0477467

(7) Jarman, R. H.; Jacobson, A. J.; Melchior, M. T. *J. Phys. Chem.* **1984**, *88*, 5748.
(8) (a) Vaughan, D. E. W. *Stud. Surf. Sci. Catal.* **1991**, *65*, 275. (b) Vaughan, D. E. W.; Strohmaier, K. G. *Microporous Mesoporous Mater.* **1999**, *28*, 233.