A Zeolitic Material with a Three-Dimensional Pore System Formed by Straight 12- and 10-Ring Channels Synthesized with an Imidazolium Derivative as Structure-Directing Agent

Mathias Dodin,[†] Jean-Louis Paillaud,*,[†] Yannnick Lorgouilloux,[†,‡] Philippe Caullet,[†] Erik Elkaïm,[§] and Nicolas Bats[#]

Equipe Matériaux à Porosité Contrôlée (MPC), Institut de Science des Matériaux de Mulhouse (IS2M), LRC CNRS 7228, Université de Haute Alsace, ENSCMu, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France, Synchrotron Soleil, L'Orme des Merisiers, Saint-Aubin BP48, 91192 Gif-sur-Yvette Cedex, France, and IFP-Lyon, BP3, 69360 Solaize, France

Received April 29, 2010; E-mail: jean-louis.paillaud@uha.fr

Abstract: IM-20 is a novel microporous germanosilicate with an interesting zeolitic structure. It has been prepared via the fluoride route with 3-butyl-1-methyl-3*H*-imidazol-1-ium as the organic structure-directing agent and its structure solved from synchrotron powder X-ray diffraction data. The chemical formula per unit cell is $Si_{42.2}Ge_{17.8}O_{120}$ under its calcined form. IM-20 possesses a new framework topology, the 3D channel system being formed by straight intersecting 12- and 10-membered rings. Two types of *d4r* composite building units are present in IM-20, their average Si/Ge molar ratio being about 8.52 or 0.56. Surprisingly, the pure silica or silica-rich units are fluoride-free in the as-synthesized material.

The search for new zeolites with original framework topologies containing larges pores (i.e., with low framework densities) is always a challenge and the object of many works around the world. The main motive is the capability for such definite microporous systems with diverse pore sizes and shapes to present specific catalytic and adsorptive properties.[1] Among the synthesis routes used by researchers, the fluoride method initially applied by Flanigen et al. for the preparation of silicalite-1 in almost neutral media,[2] which was then developed on a large scale, is of high interest. The F^- mineralizer has the advantage of leading to materials with a lower density of defects.[3] This method is also at the origin of new stable zeolites, especially in Valencia in Corma's group with the ITQ-n series of zeolites.[4] In particular, in Valencia, low amounts of water were used for the first time, which favors the crystallization of zeolites with low-density frameworks in a system leading to pure silica materials. It is worth noting that, during the same period, many new aluminosilicates of the SSZ-n family were also discovered at Chevron Texaco using the more classical alkaline route but, more recently, also via the fluoride route.[5] Another interesting recent development is the combination of the fluoride method with two different sources of framework atoms, in particular germanium and silicon atoms, which made it possible to crystallize new zeolitic topologies, many of them possessing F^--containing double four-ring (*d4r*) composite building units in their structures. It is well known that small rings such as three- and four-member rings are key to the crystallization of silica-based microporous materials with large pores.[6] In the case of germanates, the smaller rings are favored due to the longer Ge−O bond length (~1.74 Å) and smaller Ge−O−Ge angle (~130°) compared with the corresponding silicon ones (Si−O ~1.61

Å and Si−O−Si ~145°).[7] While the templating role of the F^- ion in the formation of the *d4r* unit in pure silicate was well established,[4] germanium itself promotes the formation of the *d4r* units as in, e.g., IM-12 of topology **UTL** or ITQ-33.[8,9]

Until now, the discovery of new zeolites has depended mainly on the choice of the organic structure-directing agent (OSDA) and appears to have been more or less serendipitous. Indeed, from a theoretical point of view, the design from intuition or by computation (in spite of the recent progresses) of an accurate OSDA that researchers should employ to synthesize a predicted framework or a framework existing in a different system (e.g., phosphate-based ↔ silica-based) has been successful only in very rare cases.[10−12] For this reason, we believe that the creative approach of the researchers at Chevron Texaco, which consists of building libraries of OSDAs from families of organic reactions to obtain series of substituted derivatives of interest, must be pursued.[5b,13] Accordingly, derivatives of imidazole such as 1,3-dimethyl-3*H*-imidazol-1-ium, 1,2,3-trimethyl-3*H*-imidazol-1-ium, 1,3-diisopropyl-3*H*-imidazol-1-ium, and 1-isopropyl-3-methyl-3*H*-imidazol-1-ium led to the crystallization of **TON**, **MTT**, and **MTW** types of zeolites in basic media.[14] In fluoride media, the same structures were synthesized,[5b] but in addition, 1,2,3-trimethyl-3*H*-imidazol-1-ium allowed the synthesis of ITQ-12 (**ITW**).[15] Interestingly, these OSDAs are very selective, regardless of the molecular ratio H_2O/SiO_2 of the starting synthesis gel in fluoride media.[5b] In addition, we mention here the recently published work on the synthesis of high-silica molecular sieve SSZ-70 (layered-like) using a variety of designed imidazolium derivatives to explore the nature of the OSDA/framework interactions.[16] Note that ionic liquids such as imidazolium salts have been used in the so-called iono-thermal synthesis. However, up to now, this method has not led to the formation of any silica-based porous material.[17]

In the (Si,Ge) system, the fluoride route with 3-ethyl-1-methyl-3*H*-imidazol-1-ium as the OSDA allowed us to crystallize the microporous germanosilicate IM-16 of topology **UOS**.[18] Here, we present the novel zeolite IM-20[19] of chemical formula per unit cell $Si_{42.2}Ge_{17.8}O_{120}$ in its calcined and anhydrous form, also prepared via the fluoride route with 3-butyl-1-methyl-3*H*-imidazol-1-ium (Figure 1) as the OSDA. IM-20 possesses a new framework topology, the 3D channel system being formed by 12- and 10-membered rings (12- and 10MRs).

IM-20 was hydrothermally synthesized from a gel prepared by mixing Aerosil 200 (>98% Degussa), amorphous germanium oxide GeO_2 (>99.99%, Aldrich), HF acid (40%, Carlo Erba), distilled water, and 3-butyl-1-methyl-3*H*-imidazol-1-ium bromide (98%, Solvionic), which had previously been transformed into its OH form by ion

[†] IS2M.
[§] Synchrotron Soleil.
[#] IFP-Lyon.
[‡] Present address: Katholieke Universiteit Leuven, Centrum voor Oppervlak-techemie en Katalyse, Kasteelpark Arenberg 23, 3001 Heverlee, Belgium.
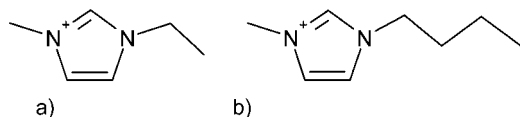
Figure 1. (a) 3-Ethyl-1-methyl-3H-imidazol-1-ium and (b) 3-butyl-1-methyl-3H-imidazol-1-ium.

exchange in water (Dowex SBR LC NG, OH Form (Supelco)). The gel composition was 0.6 SiO_2:0.4 GeO_2:0.5 OSDA(OH):0.5 HF:10 H_2O (pH $\approx$ 8). The structure of IM-20 was solved from a synchrotron powder X-ray diffraction pattern of the calcined product. It was indexed in an orthorhombic unit cell with $a = 25.165(6)$ Å, $b = 12.701(2)$ Å, and $c = 11.601(1)$ Å using the indexing algorithms DICVOL.[20] The analysis of the systematic extinctions suggested the possible space groups $P222$ (No. 16), $Pmm2$ (No. 25), or $Pmmm$ (No.47). The crystal structure was then solved by direct methods applied on the extracted intensities using the program EXPO2004[21] with the highest symmetry ($Pmmm$) and refined with the GSAS package[22,23] (see Supporting Information for details).

The asymmetric unit of calcined IM-20 contains 10 crystallograpically independent T-sites, and the Rietveld refinement indicates that no T-site is purely siliceous. The chemical composition of the inorganic framework per unit cell achieved after the refinement is $[Si_{42.2}Ge_{17.8}O_{120}]$, which closely matches that obtained by chemical analysis of the as-made product $|(C_8N_2H_{15})_3|[Si_{42.2}Ge_{17.8}O_{120}F_2OH]$ [see the Supporting Information for details]. On the ^{19}F MAS NMR spectrum of as-made IM-20 (Figure 2), only a single asymmetric signal at about -8.9 ppm is present (Figure 2), in spite of the presence of two distinct $d4r$'s found by the crystallographic study. There is no signal in Figure 2 indicating the presence of fluoride in other sites than inside the $d4r$ units. There are one (T1-$d4r$) and two (T2,T3-$d4r$) per unit cell of IM-20. The first type of $dr4$ is defined by T1 atoms only (T1-$d4r$) with a Si/Ge molar ratio of about 8.52, i.e. some of those cages would contain only Si atoms, while others will have one or two Ge atoms. Previous ^{19}F MAS NMR studies on germanosilicates for which F^- are located at the center of a $d4r$ of chemical composition 8Si, (7Si,1Ge), or (6Si,2Ge) showed that the corresponding signals are normally observed at about -38, -20, and -19 ppm, respectively.[24] The second type of $d4r$ responsible for the signal observed at -8.9 ppm is defined by four T2 and four T3 sites (T2,T3-$d4r$), the average composition being about (5Ge,3Si) per $d4r$ unit.[24] F^- anions located in such $d4r$ units usually give rise to a signal around -9 ± 1 ppm.[24] By taking into account the
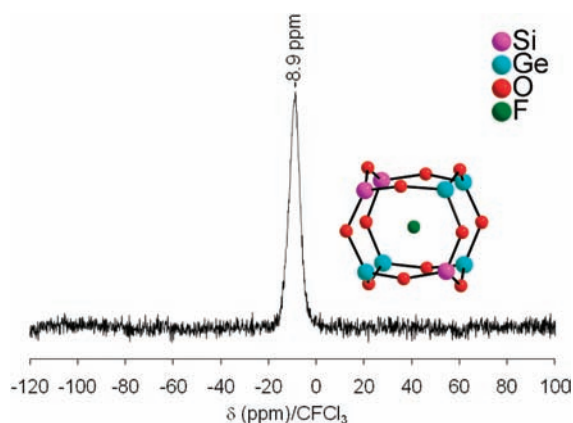

Figure 2. ^{19}F MAS NMR spectrum of as-made IM-20. The inset represents a F^--containing $d4r$ unit with a possible distribution of the Si and Ge elements responsible for the single resonance at -8.9 ppm.
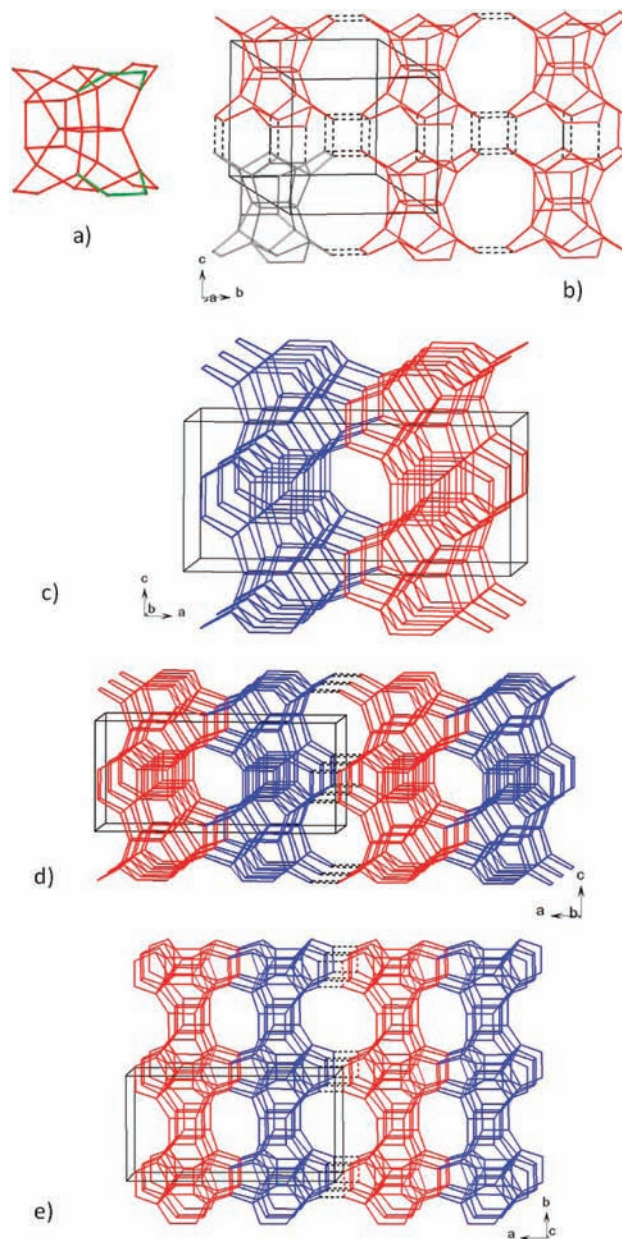
Figure 3. Building scheme of IM-20: (a) T32 unit consisting of a T28 unit (red) of the **ITR** topology plus four additional T atoms (green); (b) layer viewed along a; (c) PerBU viewed along b; and connection mode viewed (d) along b and (e) along c. The dotted bonds are the connecting bonds between units; the oxygen atoms have been omitted for clarity.

chemical analysis and the ^{19}F MAS NMR results, only the two (T2,T3-$d4r$) cubic units are occupied by one fluoride anion, the T1-$d4r$ unit being fluoride-free. The three positively charged OSDAs are compensated by two fluoride anions and one occluded OH^- species or by two F^- together with a defect probably located on the T1 site ($(T-O)_3Si1-O^-$ $HO-Ge1(O-T)_3$ or $(T-O)_3Ge1-O^-$ $HOSi1(O-T)_3$). If the second hypothesis is true, the defects disappear after dehydroxylation during the calcination under a dry atmosphere.

The structure of the new zeolite IM-20 can be described using convenient units containing 32 T atoms or T32 units. Like in ITQ-34 (**ITR**),[25] this building unit consists of two *mel* and one *stf* composite building units (CBUs) sharing four rings (T28 unit in ITQ-34)[26] but with four additional T atoms present in the case of IM-20 (Figure 3a). The stacking mode is different here, as T32 units related along b and c by pure translations are connected through 4MRs (and 6MRs) into
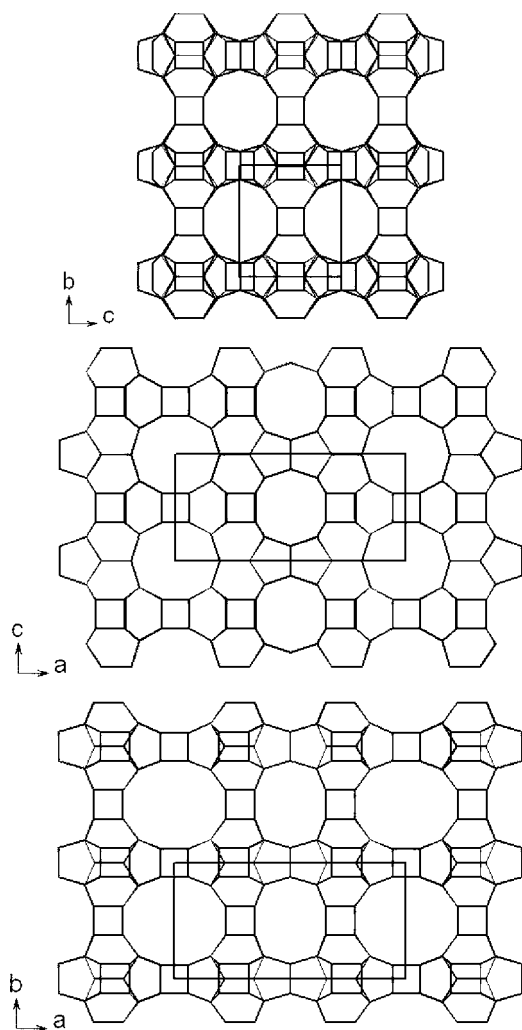
unclear, but it was shown recently on ITQ-21 that at the early stages of the synthesis, no fluoride ions are occluded inside the *d4r* units, and it is suggested that they are incorporated later during the synthesis.[27] For IM-20, a charge compensating defect located within the silica rich *d4r* CBUs could also explain this absence.

Supporting Information Available: Details on ^{19}F MAS NMR, chemical analyses, N_2 adsorption, synchrotron data collection, and structure determination of IM-20 (CIF file included). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Yu, J. In *Introduction to Zeolite Science and Practice*; Èejka, J., van Bekkum, H., Corma, A., Schüth, F., Eds.; Studies in Surface Science and Catalysis *168*; Elsevier: Amsterdam, 2007; pp 39−103.

(2) Flanigen, E. M.; Patton, R. L. US Patent 4,073,865, 1978; *Chem. Abstr.* **1978**, *88* 138653. (b) Guth, J.-L.; Kessler, H.; Wey, R. In *New Developments in Zeolite Science and Technology*; Murakami, Y., Iijima, A., Ward, J. W., Eds.; Studies in Surface Science and Catalysis *28*; Elsevier: Amsterdam, 1986; pp 121−128.

(3) Caullet, P.; Paillaud, J.-L.; Simon-Masseron, A.; Soulard, M.; Patarin, J. *C. R. Chim.* **2005**, *8*, 245−266.

(4) (a) Camblor, M. A.; Villaescusa, L. A.; Díaz-Cabañas, M. J. *Top. Catal.* **1999**, *9*, 59–76. (b) Villaescusa, L. A.; Camblor, M. A. *Recent Res. Dev. Chem.* **2003**, *1*, 93–141. (c) Corma, A.; Davis, M. E. *ChemPhysChem* **2004**, *5*, 304–313.

(5) (a) Burton, A. W.; Zones, S. I.; Elomari, S. *Curr. Opin. Colloid Interface Sci.* **2005**, *10*, 211–219. (b) Zones, S. I.; Hwang, S.-J.; Elomari, S.; Ogino, I.; Davis, M. E.; Burton, A. W. *C. R. Chim.* **2005**, *8*, 267–282. (c) Burton, A. W.; Lee, G. S.; Zones, S. I. *Microporous Mesoporous Mater.* **2006**, *90*, 129–144.

(6) Brunner, G. O.; Meier, W. M. *Nature* **1989**, *337*, 146–147.

(7) O'Keeffe, M.; Yaghi, O. M. *Chem.—Eur. J.* **1999**, *5*, 2796–2801.

(8) Paillaud, J.-L.; Harbuzaru, B.; Patarin, J.; Bats, N. *Science* **2004**, *304*, 990–992.

(9) Corma, A.; Díaz-Cabañas, M.-J.; Jordá, J. L.; Martínez, C.; Moliner, M. *Nature* **2006**, *443*, 842–845.

(10) Delprato, F.; Delmotte, L.; Guth, J. L.; Huve, L. *Zeolites* **1990**, *10*, 546.

(11) Schmitt, K. D.; Kennedy, G. J. *Zeolites* **1994**, *14*, 635–642.

(12) For a review of template design see: Lewis, D. W. In *Computer Modelling of Microporous Materials*; Catlow, C. R. A., van Santen, R. A., Smit, B., Eds.; Elsevier B.V.: Amsterdam, 2004; Chapter 8, pp 243−265.

(13) For a study of piperidinium derivatives as OSDAS in pure silica zeolite synthesis see: Zones, S. I.; Burton, A. W.; Lee, G. S.; Olmstead, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 9066–9079.

(14) Zones, S. I. *Zeolites* **1989**, *9*, 458–467.

(15) Barrett, P. A.; Boix, T.; Puche, M.; Olson, D. H.; Jordan, E.; Köller, H.; Camblor, M. A. *Chem. Commun.* **2003**, 2114–2115.

(16) Archer, R. H.; Zones, S. I.; Davis, M. E. *Microporous Mesoporous Mater.* **2010**, *130*, 255–265.

(17) Parnham, E. R.; Morris, R. E. *Acc. Chem. Res.* **2007**, *40*, 1005–1013.

(18) Lorgouilloux, Y.; Dodin, M.; Paillaud, J.-L.; Caullet, P.; Michelin, L.; Josien, L.; Ersen, O.; Bats, N. *J. Solid State Chem.* **2009**, *182*, 622–629.

(19) Dodin, M.; Lorgouilloux, Y.; Paillaud, J.-L.; Caullet, P.; Patarin, J.; Bats, N. French patent FR 2940266.

(20) Boultif, A.; Louër, D. *J. Appl. Crystallogr.* **1991**, 987–993.

(21) (a) Altomare, A.; Burla, M. C.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G. *J. Appl. Crystallogr.* **1995**, *28*, 842–846. (b) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G. J.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(22) (a) Larson, A. C.; Von Dreele, R. B. *General Structure Analysis System*; Report LAUR 86-748; Los Alamos National Laboratory: Los Alamos, NM, 2000. (b) Toby, B. H. *J. Appl. Crystallogr.* **1994**, *34*, 210–213.

(23) IM-20 orthorhombic, *Pmmm*, $a = 25.1611(5)$ Å, $b = 12.7013(1)$ Å, $c = 11.6001(1)$ Å, $V = 3707.15(9)$ Å^3, $wR_p = 0.0432$ for 1509 observations.

(24) (a) Blasco, T.; Corma, A.; Díaz-Cabañas, M.-J.; Rey, Fernando; Vidal-Moya, J. A.; Zicovich-Wilson, C. M. *J. Phys. Chem. B* **2002**, *106*, 2634–2642. (b) Wang, Y.; Song, J.; Gies, H. *Solid State Sci.* **2003**, *5*, 1421–1433.

(25) Corma, A.; Diaz-Cabanas, M. J.; Jorda, J. L.; Rey, F.; Sastre, G.; Strohmaier, K. G. *J. Am. Chem. Soc.* **2008**, *130*, 16482–16483.

(26) Baerlocher, Ch.; Meier, W.; Olson, D. H. *Atlas of Zeolite Framework Types*, sixth ed.; Elsevier, Amsterdam, 2007. Available from: http:// www.iza-structure.org/databases/.

(27) Schaack, B. B.; Schrader, W.; Corma, A.; Schuth, F. *Chem. Mater.* **2009**, *21*, 4448–4453.

Figure 4. Projections of the IM-20 structure along (top) [100], (middle) [010], and (bottom) [001]. The oxygen atoms have been omitted for clarity.

the layer as in Figure 3b. This connection mode generates *lau* and *d4r* (T2,T3-*d4r*) CBUs. Two layers related by a mirror plane parallel to (*b*,*c*) are then fused sharing the 4MRs of the *stf* CBUs to form a periodic building unit, or PerBU (Figure 3c). The full structure is obtained by connecting through 4MRs these PerBUs related along *a* by a pure translation as illustrated in Figure 3d,e. A second type of *d4r* CBUs (T1-*d4r*) is thus created.

The 3D channel system of IM-20 is formed by straight intercrossing 12MR (Figure 3e) and 10MR channels. 12MR (7.7 Å × 6.1 Å) and 10MR (5.8 Å × 4.2 Å) channels are parallel to the *c*-axis, two different types of 10MR channels (5.9 Å × 5.0 Å and 5.0 Å × 4.2 Å) are parallel to the *b*-axis, and a third kind of 10MR channels (5.8 Å × 5.0 Å) lie along the *a* axis (Figure 4).

The pore system of IM-20 is in good agreement with the pore volume obtained from N_2 adsorption measurement. The calculated microporous volume is 0.16 cm³/g (about 0.2 cm³/g for the hypothetical pure silica IM-20) and corresponds to a large-pore zeolite.

In summary, IM-20 is a novel germanosilicate with an interesting new zeolite topology that is stable after calcination under a dry atmosphere. The 3D pore system is new and consists of four different types of 10MR and one 12MR straight channels. Note that pure silica or silica-rich and fluoride-free *d4r* CBUs are present in the as-synthesized IM-20 molecular sieve. The reason for the presence or absence of fluoride ions in the germanium-containing *d4r* units remains