Towards a Rational Synthesis of Large-Pore Zeolite-Type Materials?

Duncan E. Akporiaye*

Until ten years ago, one of the main goals in the synthesis of zeolites and related crystalline microporous materials was the preparation of materials whose structures contain "large" and "extra-large" pores with dimensions equal to or greater than 12 T atoms (≥ 0.75 nm, T = tetrahedral framework cation). This search was driven by, among others, the desire to find replacements for the ubiquitous faujasite structure with 12-ring pores, as well as to generate new applications in catalysis, adsorption, and ion exchange. The determination of the structures of VPI-5 (18-ring) and $AlPO_4$-8[1] (14-ring) presaged the discovery of the range of aluminophosphate structures with extra-large pores listed in Table 1. The subsequent finding of a new class of ordered mesoporous materials, prepared by using surfactant-based structure-directing agents,[2] might have invalidated the above approach to very large pore materials, since they extended the range of pore sizes achievable from approximately 1.8 nm to greater than 20 nm. However, these ordered mesoporous materials have found few catalytic applications owing to the weak acidity of the aluminosilicate variants.

Table 1. Overview of zeolite-type materials with extra-large pores.

Pore size no. of T atoms	Aluminophosphate-based	Alumino-silicate-based
20	Cloverite[1] JDF-20[13]	–
18	VPI-5[1]	–
16	ULM-16[14]	–
14	$AlPO_4$-8[1]	UTD-1[5] CIT-5[6]

The recent trend to develop rational synthetic strategies can provide a means for the discovery of new large-pore zeolite-type structures. This is well illustrated by the extensive work of Zones et al.[3] on the synthesis of high-silica zeolites, which is based on understanding the role and interaction of the organic structure-directing agent (guest) in the gel chemistry, and the final crystalline structures (host) in terms of a host–guest relationship. Thus, in the hunt for high-silica materials with multidimensional channel systems, bulky polycyclic organic amines were used to give maximum stabilization of the hydrophobic inner silica surface of these compounds. Large-pore materials such as SSZ-31 (12-ring)[4] are the fruits of this work; however, the recent determination of the structure of this material also reveals the likely limitations of this approach. In the choice of bulky organic amines, the trend is towards low charge density on the organic compound and in the framework (high Si/Al ratio). With this strategy, it is evident that the organic compound will increasingly act as an inert space filler, and the challenge for the synthetic zeolite chemist will be to maximize the impact of the shape of the structure-directing agent on the structure of the product. The result of this is a tendency for the formation of one-dimensional channel systems and highly intergrown mixtures of polymorphs with closely related structures.

This trend is also evident in the novel conditions employed in the synthesis of the only two known 14-ring zeolites, UTD-1[5] (Figure 1) and CIT-5.[6] The former involves a bis-cyclopentadienyl complex of cobalt, and the latter is critically dependent on the presence of lithium in addition to the polycyclic amine.

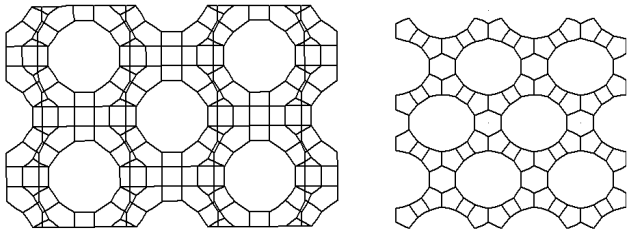

Figure 1. Structures of UCSB-8 and UTD-1.

In spite of these perceived limitations, the convergence of these experimental approaches with newly developed computational strategies may provide further breakthroughs. Thus, quantitative shape analysis of the guest and host[7] following energy minimization of the organic molecule in a wide range of zeolite frameworks gives some insight into the relationship between shape and size. Following naturally from this, in a revolutionary development, the de novo design of the guest molecule[8] was implemented with algorithms that maximize the stabilizing overlap of the van der Waals surfaces of the host and guest by means of the directed "growth" of the organic compound within the confines of the pore system.

In recent exciting work by Stucky et al.,[9] an alternative strategy for the preparation of large-pore, multidimensional structures led to a range of novel metalloaluminophosphate

[*] Dr. D. E. Akporiaye
Sintef Applied Chemistry
P.O. Box 124 Blindern, N-0314 Oslo (Norway)
Fax: (+47) 22067350
E-mail: duncan.akporiaye@chem.sintef.no

  1433-7851/98/3718-2456 $ 17.50+.50/0

structures. The basis of this new approach is in essence diametrically opposed to the routes used so far for aluminosilicate systems, and preliminary results appear to confirm a degree of rational design. Instead of reducing the charge density on the organic structure-directing agent through the use of bulky molecules, with the consequent weakening of the electrostatic interaction between host and guest, the approach of charge-density matching of host and guest has been introduced. Thus, following the analysis of known zeolite systems in which large multidimensional pores are associated with low Si/Al ratios and hence high framework charge density, the goal has been to use organic compounds with the desired high charge density. Diamines of the general formula $H_2N(CH_2)_nNH_2$ proved fruitful in this role and led to three novel structures UCSB-6, UCSB-8 (Figure 1), and UCSB-10 in a metalloaluminophosphate system in which, for the first time, aluminum is replaced to a large extent by cobalt, magnesium, manganese, and zinc in the tetrahedral structure. The hydrophobic hydrocarbon backbone of these diamines is believed to allow the separation of the charged inorganic wall from the cage/pore contents. This indicates a form of "self-assembly" during the crystallization of this system, in which the strong interaction between the inorganic species and the protonated amino groups at the end of the long hydrocarbon backbone direct the formation of large pores. If this mechanism is valid, it would point to an interesting correspondence with the charge-matching concepts that describe the formation of MCM and related mesoporous systems.[10, 11]

A natural progression following the success of this approach in preparating UCSB-*x* materials is to consider how this might now be applied to the aluminosilicate system, for which few structures with extra large pores are known (Table 1). This is important for the industrial application of this important class of acid catalysts and sorbents, since few aluminophosphate-type microporous materials have sufficient thermal stability to be used in commercial processes.[12] This is in contrast to the high thermal stability and extensive application of zeolites in refinery and petrochemical processes.

German version: *Angew. Chem.* **1998**, *110*, 2594 – 2595

Keywords: microporosity · synthesis design · zeolites · zeolite anologues

[1] W. M. Meier, D. H. Olson, C. Baerlocher, *Atlas of Zeolite Structure Types*, Elsevier, Boston, MA, **1996**.
[2] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710 – 712.
[3] S. I. Zones, Y. Nakagawa, L. T. Yuen, T. V. Harris, *J. Am. Chem. Soc.* **1996**, *118*, 7558 – 7567.
[4] R. F. Lobo, M. Tsapatsis, C. C. Freyhardt, I. Chan, C.-Y. Chen, S. I. Zones, M. E. Davis, *J. Am. Chem. Soc.* **1997**, *119*, 3732 – 3744.
[5] R. F. Lobo, M. Tsapatsis, C. C. Freyhardt, S. Khodabandeh, P. Wagner, C.-Y. Chen, K. J. Balkus, S. I. Zones, M. E. Davis, *J. Am. Chem. Soc.* **1997**, *119*, 8474 – 8484.
[6] P. Wagner, M. Yoshikawa, M. Lovallo, K. Tsuji, M. Taspatsis, M. E. Davis, *Chem. Commun.* **1997**, *22*, 2179 – 2180.
[7] R. E. Boyett, A. P. Stevens, M. G. Ford, P. A. Cox, *Zeolites* **1996**, *17*, 505 – 512.
[8] D. J. Willock, D. W. Lewis, C. R. A. Catlow, G. J. Hutchings, J. M. Thomas, *J. Mol. Catal.* **1997**, *119*, 415 – 424.
[9] X. Bu, P. Feng, G. D. Stucky, *Science* **1997**, *278*, 2080 – 2085
[10] Q. Huo, R. Leon, P. M. Petroff, G. D. Stucky, *Science* **1995**, *268*, 1324 – 1327.
[11] P. Behrens, *Angew. Chem.* **1996**, *108*, 561 – 564; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 515 – 518.
[12] B. V. Vora, T. L. Marker, P. T. Barger, H. E. Fullerton, H. R. Nilson, S. Kvisle, T. Fuglerud, *Stud. Surf. Sci. Catal.* **1997**, *107*, 87 – 98.
[13] R. H. Jones, J. M. Thomas, J. S. Chen, R. R. Xu, Q. S. Huo, S. G. Li, Z. Ma, *J. Solid State Chem.* **1993**, *102*, 202 – 208.
[14] T. Loiseau, G. Ferey, *J. Mater. Chem.* **1996**, *6*, 1073 – 1074.

  1433-7851/98/3718-2457 $ 17.50+.50/0