The Quest for Extra-Large Pore, Crystalline Molecular Sieves

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Abstract: The definition and reasons for desiring extra-large pore, crystalline molecular sieves are ennumerated. A historical perspective on the development of these materials is presented with emphasis on critical features important for practical application. Based on the known physiochemical properties of extra-large pore materials, several avenues for their synthesis are suggested. Finally, a few issues of concern when dealing with this class of materials are presented.

Keywords: large-pore materials · materials science · molecular sieves · zeolites

Introduction

Zeolites and zeolite-like materials comprise a broad range of microporous, crystalline solids whose main uses are as adsorbents, ion-exchangers, and catalysts. These solids have tunable properties such as pore size, shape, and capacity, and lead one to believe that designer catalysts may someday be possible through the molecular engineering of these structures. Zeolites are constructed from the tetrahedral units SiO_4 and AlO_4, which connect to form crystalline structures of composition $M_x \cdot (Si_{1-x} + Al_x)O_2 \cdot yH_2O$, where M is a monovalent cation, y is the amount of occluded water, and $0 \leq x \leq 0.5$. These materials contain complex pore networks that can be used to sort molecules.

Figure 1 illustrates framework structures and pore sizes for three zeolites: CaA, ZSM-5, and NaX. When using this representation for the structures, the straight line segments denote bridging oxygen atoms, and their intersection points the silicon and aluminum atoms. Zeolites with 8, 10, and 12 oxygen atoms (likewise 8, 10, and 12 silicon + aluminum atoms) used to contruct the rings of the pores are called small-, medium-, and large-pore materials, respectively. Thus CaA, ZSM-5, and NaX are small-, medium-, and large-pore zeolites with pore sizes of approximately 4.5, 6, and 8 Å, respectively (defined by means of adsorption experiments as well as from crystal structure data).

In 1982, Wilson and co-workers[1] disclosed a new class of zeolite-like molecular sieves that comprised AlO_4 and PO_4 tetrahedra. These phosphate-based, crystalline molecular sieve materials provide a wealth of new structures (see Figure 1) not observed in zeolites (in addition to several that are structural analogues). Additionally, a large variety of element combinations successfully form phosphate-based materials (e.g. $AlPO_4$, $GaPO_4$ etc).[2]

Prior to 1987, all zeolite and zeolite-like molecular sieves contained large pores (12 oxygen atoms) or smaller. Thus, the pore sizes were all below 10 Å. In spite of this boundary, zeolites have revolutionized the oil and chemical industries since the 1950's.[3,4] Zeolites are used in many applications as catalysts, for example, catalytic cracking, synthesis of ethylbenzene and cumene from benzene and ethylene or propylene, respectively. One of the hallmark features of molecular sieve-based catalysis is the ability to perform shape-selective reactions. Figure 2 illustrates reaction shape-selectivity using medium- (ZSM-5, TS-1) and large-pore (ZSM-12, Ti-β) molecular sieve catalysts. The alkylation reactions shown in Figure 2 can be accomplished with *para*-isomer selectivities of greater than 90%. For the epoxidation reactions listed, the yields of the epoxides are greater than 95% (the reaction of cyclooctene can not be accomplished with TS-1 because the pore size is too small to allow the olefin to enter; i.e., discrimination between olefins on the basis of size).

The availablity of zeolites and zeolite-like materials with pore sizes of 10–20 Å should open new catalytic chemistry in the petrochemical and life-sciences fields. Because of the lack of materials with uniform pore size in the 10–20 Å region, and because of the great desire to perform shape-selective adsorption/separations and catalysis on molecules in this size range (the movement to liquid-phase reactions and conversions involving fine chemicals and pharmaceuticals is occurring), there has been a standing goal to prepare zeolite and zeolite-like molecular sieves with pores consisting of greater than 12 oxygen atoms. We proposed to call molecular sieves that contain ring sizes above 12 extra-large pore materials.[8] It was not until 1987 that an extra-large pore material was prepared, namely, VPI-5.[9] VPI-5 has set the stage for the development of numerous other extra-large pore materials.

Discussion

History of Extra-Large Pore Materials: Like so many other pioneering ideas and concepts in molecular sieve science and technology, Richard Barrer and his collaborators were the first

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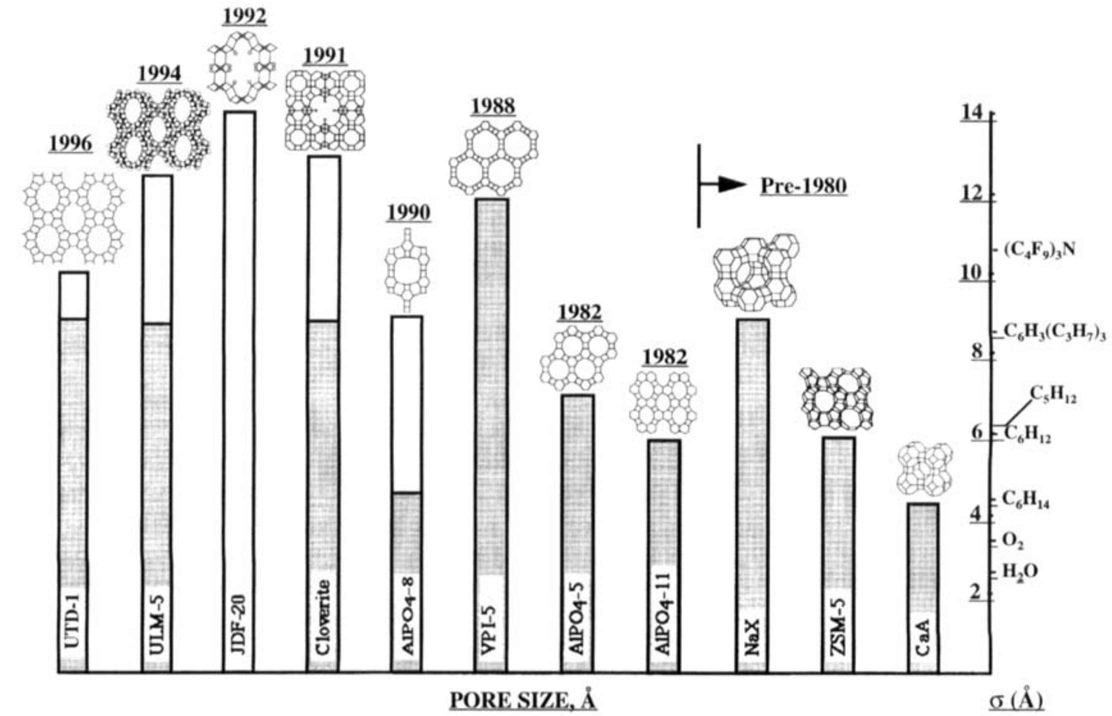

Figure 1. Correlation between pore size of molecular sieve as measured from the crystal structure (top of bar) and adsorption studies (top of shaded region in each bar) and the kinetic diameter (σ) of various molecules.

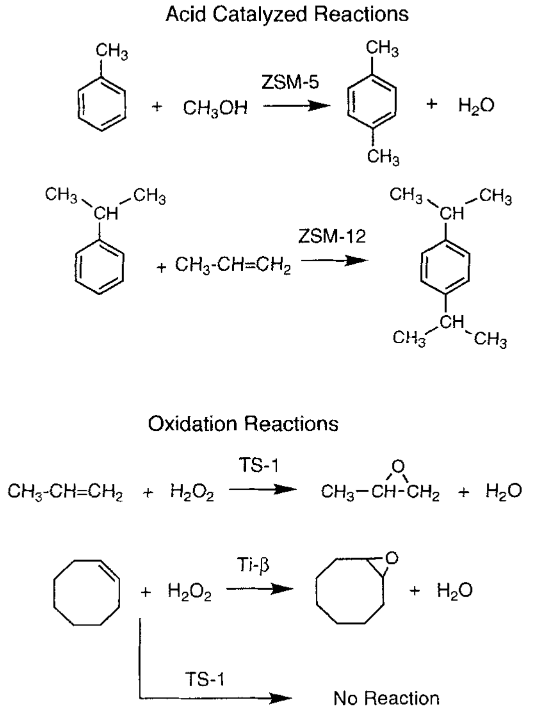

Figure 2. Reactions illustating shape-selectivity in medium- (ZSM-5 [3], TS-1 [5]) and large-pore (ZSM-12 [6], Ti-*β* [7]) materials.

to report on the idea of preparing extra-large pore materials.[10] Barrer and Villiger presented a series of hypothetical structures related to zeolite L (large pore) that had 24 membered ring (24MR) pores with a free diameter of approximately 15 Å. Some of these networks consisted of known local atomic arrangements that do not violate crystal chemistry constraints, for example, bond lengths and angles (the model having a hexagonal unit cell of $a = 22$ Å, $c = 7.5$ Å gives a satisfactory distance least-squares refinement (DLS-76[11]) of the atomic positions). Subsequently, other hypothetical, extra-large pore networks were reported. For example, Smith and Dytrych illustrated several nets with channels of unlimited diameter.[12] Figure 3 shows an example of one of these nets. The net that is comprised of all 6MR's is the topology of $AlPO_4$-tridymite. Insertion of a 4MR between the 6MR's gives a net that contains a 12MR and is the topology of $AlPO_4$-5. Subsequent insertion of a 4MR adjacent to each 4MR in $AlPO_4$-5 gives a net that has an 18MR and was subsequently shown to possess the topology of VPI-5.[9]

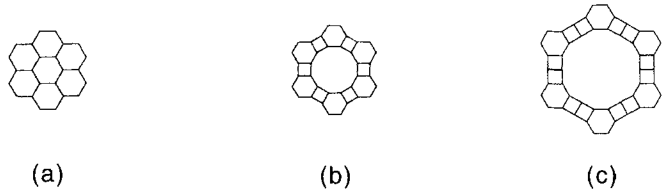

Figure 3. Schematic framework [001] projections of $AlPO_4$-tridymite (a), $AlPO_4$-5 (b), and VPI-5 (c).

In addition to hypothetical, extra-large pore networks, the structure of an extra-large pore material, the mineral cacoxenite, was reported by Moore and Shen in 1983 and contained a channel of 15 Å diameter.[13] Cacoxenite is a hydrated, basic, ferric oxyphosphate mineral, which has yet to be synthesized. Additionally, it possesses iron octahedra, and structural (OH) and H_2O groups: $[Al(Al,Fe)_3Fe_{21}O_6(OH)_{12}(PO_4)_{17}(H_2O)_{24}]$.[13] Thus, it is not a network containing only oxide tetahedra as are zeolites. Cacoxenite is not able to function as an adsorbent or catalyst because the structure collapses upon heating to remove the water occluded within the pore network.

By the mid-1980's, hypothetical extra-large pore nets were known, phosphate-based molecular sieves were known, and the structure of the 15 Å pore, phosphate-containing mineral cacoxenite was known. Thus, it is not surprising that the first extra-large pore material, VPI-5, is a phosphate-based material, namely, an aluminophosphate. After the discovery of VPI-5, numerous phosphate-based, extra-large pore materials were prepared. Table 1 summarizes these materials. All of these solids except UTD-1 and TPA-SnS-3 are phosphate-based molecular sieves. Although the materials listed in Table 1 all have extra-large rings in their as-synthesized form, some of these materials decompose upon attempts to remove occluded material (mostly organic molecules) from their void spaces (e.g. JDF-20), or have limited thermal stability that make their use as a molecular sieve difficult. This is not surprising in view of the fact that all the materials listed in Table 1 except UTD-1 have at least one of the following features: mixed metal-ion coordinations (e.g., octahedral/tetrahedral aluminum), terminal (OH) groups and other nontetrahedral framework groups (e.g., OH, H_2O, F), that like in cacoxenite lead to low stability relative to zeolites. For example, the as-synthesized form of VPI-5 possesses octahedral and tetrahedral aluminum. The octahedral aluminum is in the center of the so-called triple crankshaft chains that make up the fused four-membered rings (see Figure 4a). The dehydrated triple crankshaft chain is very strained and the hydration and coordination change (tetrahedral to octahedral) releases this strain. If the water from as-synthesized VPI-5 is not carefully removed, it can assist in the transformation of VPI-5 to $AlPO_4$-8 by participating in the hydrolysis of Al–O–P linkages (see Figure 4b). Because the reorganization of the VPI-5 structure occurs randomly, the $AlPO_4$-8 thus formed has a high degree of stacking disorder endowing it with a very low adsorption capacity.

Table 1. Summary of extra-large pore materials.

Material	Year reported	Main framework composition	Ring size (O atoms)	Pore size [a]	Ref.
VPI-5	1988	$AlPO_4$	18	13	[9]
$AlPO_4$-8	1990	$AlPO_4$	14	<10	[14,15]
Cloverite	1991	$GaPO_4$	20	<10	[16]
JDF-20	1992	$AlPO_4$	20	– [c]	[17]
ULM-5	1994	$GaPO_4$	16	NR [d]	[18]
AlMepO-β	1995	$Al_2(CH_3PO_3)_3$	18	6	[19]
TPA-SnS-3	1995	Sn_4S_9	32 [b]	NR	[20]
not named	1996	$V_5O_9(PO_4)_2$	16	NR	[21]
ULM-16	1996	$GaPO_4$	16	NR	[22]
UTD-1	1996	SiO_2	14	10	[23]
ULM-15	1997	$FePO_4$	16	NR	[24]

[a] In Å; proven by adsorption. [b] Contains a total of 32 atoms. [c] Collapse upon activation. [d] NR: not reported.

The practical value of phosphate-based extra-large pore materials is limited by their poor thermal and hydrothermal stability compared to zeolites. Thus, the desire for extra-large pore zeolites is high and the preparation of UTD-1 proves that the formation of extra-large pore materials is not limited to nontetrahedral frameworks and phosphate-based materials. UTD-1 is a high-silica zeolite possessing only tetrahedral atoms of silicon and aluminum and is thermally stable like other known zeolites.[23] UTD-1 shows that an extra-large pore material can have the stability necessary for commercial application.

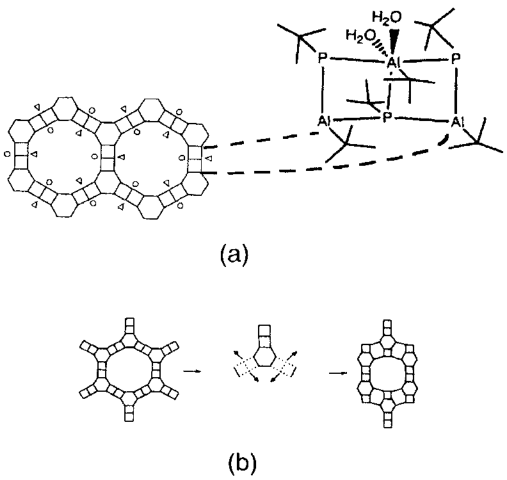

Figure 4. Structure of as-synthesized VPI-5 illustrating the octahedral aluminum (a). Transformation of VPI-5 to $AlPO_4$-8 (b). Each symbol adjacent to the center of the fused 4-ring represents two water molecules bonded to an Al atom, and indicates water molecules at different layers due to the alternation of Al and P in the framework.

Stability: After the discovery of VPI-5, it was found that this material has limited thermal and hydrothermal stability.[25] Because of the instability of VPI-5, concern was raised over whether all extra-large pore materials would possess this feature. My co-workers and I have spent much effort addressing the origin of the instability of VPI-5 and clearly the reasons enumerated above are important (ref. [25] and references therein). Thus, it could be argued that the lack of stability in VPI-5 is not due to the presence of the extra-large ring, but rather to the nature of the structural units, for example, the strained, fused four-membered rings. UTD-1 proves this premise. UTD-1 contains structural units observed in other high-silica zeolites and possesses 14MR's. The thermal and hydrothermal stability of UTD-1 is not diminished from large-pore, high-silica zeolites,[23] thus supporting the premise that the extra-large ring is not the cause of the destabilization in the other extra-large pore materials. Rather, the lack of stability is due to other structural features as mentioned above.

Methods for New Synthesis: The preparation of VPI-5 and UTD-1 set the precedence for the existence of extra-large pore molecular sieves and zeolites, respectively. There continues to be a great desire for extra-large pore materials, especially silica-based ones now that the stability of such a material is proven. UTD-1 begins to approach the pore size of interest, 10–20 Å, but there is a need for larger pores.

One approach to the synthesis of extra-large pores is through the use of large, organic, structure-directing agents. In the synthesis of high-silica materials that are somewhat hydrophobic, water-soluble organic molecules, such as quaternary ammonium compounds, can be used to organize the inorganic components into an as-synthesized, organic–inorganic composite material. For more details on this, see refs. [26,27]. Removal of the organic component, most typically by combustion in air, opens the pore space of the high-silica zeolite. The problem with preparing large organic molecules for this use is their solubility in water.[28] The molecule used to prepare UTD-1 is bis(pentamethylcyclopentadienyl)cobalt(III) hydroxide, and it has sufficient solubility in water at 175 °C to act as a structure-directing agent. Thus, this route to extra-large pore materials is viable but will rely on skillful preparation of organics. For example, the polymer shown in Figure 5a is known to structure-direct the formation of large-pore zeolites such as gmelinite[29] and ZSM-12.[30] This polyelectrolyte is quite water-soluble. One approach to preparing structure-directing agents for extra-large pore zeolites could be to replace the DABCO unit (each bridge contains two methylenes) with a larger moiety as illustrated in Figure 5b. This expansion in size from the DABCO unit was insufficient in impeding the structure-direction of gmelinite and ZSM-12 (Davis et al., not reported). Thus, larger moieties like those illustrated in Figure 5c will be necessary to produce extra-large pore zeolites.

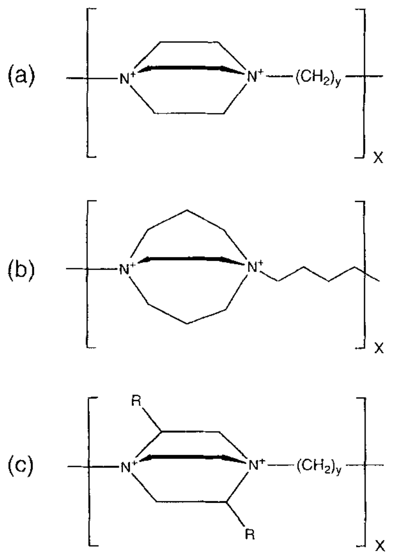

Figure 5. Polycation polymers: a) DABCO-based polymer used to prepare gmelinite and ZSM-12, b) polymer also capable of producing gmelinite and ZSM-12, and c) suggested class of new polymers for structure-directing extra-large pore materials.

In addition to the use of large structure-directing agents, there is another possibility that may lead to extra-large pore materials. Brunner and Meier have shown that there is a correlation between the minimum framework density (FD) defined as the number of tetrahedral atoms per cubic nanometer and the smallest ring size in the framework. The minimum known FD is 12.5 and is from a structure that consists of ring sizes of four (4MR's) or larger. Meier speculated that all extra-large pore structures that are based on 4MR's will have one-dimensional channel systems.[32] This is because hypothetical frameworks with multidimensional, extra-large channels yield FD's below 12. However, this boundary on FD is lowered to below 10 if the frameworks are based on 3MR's. Challenged by these ideas, we began a program to purposefully prepare materials with 3MR's. Based on the facts that zincosilicate minerals contain 3MR's and zinc is a cheap and abundant element that is not toxic (beryllium-containing silicates also possess 3MR units[33]), we initiated work on the synthesis of microporous zincosilicates.[33, 34] Thus far, we have prepared four crystalline, microporous zincosilicates that contain 3MR's. However, the largest pore size of these solids is a 9MR. We believe that this area of research deserves further attention.

In our investigation on the preparation of zincosilicates, we synthesized a new material we denoted as VPI-8.[35] VPI-8 is a high-silica molecular sieve that requires the presence of zinc for its preparation. Instead of creating 3MR's, the presence of zinc formed a new atomic arrangement we denoted as the "pinwheel" building unit (because of the arrangement of the 5MR's in the shaded area in Figure 6). Note that the 12MR large-pore of VPI-8 is constructed of four "pinwheel" units connected together. By simple insertion of 4MR's between the "pinwheel" units in a manner similar to that of Smith and Dytrych for the hexagonal nets shown in Figure 3, extra large pore nets can be formed (see Figure 6). It is unlikely that the 18MR and 20MR nets could be realized because of the presence of the fused four-membered rings (VPI-5 has this feature, but it is able to do so because it is an $AlPO_4$ that allows for octahedral coordination of Al). However, the 14MR and 16MR nets appear feasible. It is important to note that unlike other building units, the "pinwheel" unit can only construct nets of 12MR's or larger. Thus, it is well-suited to form extra-large pore structures. Note also that these nets all have one-dimensional channels as predicted by Meier for nets lacking 3MR's. A suggested strategy for preparation of these extra-large pore materials would be the use of zincosilicate chemistry and large, organic structure-directing agents.

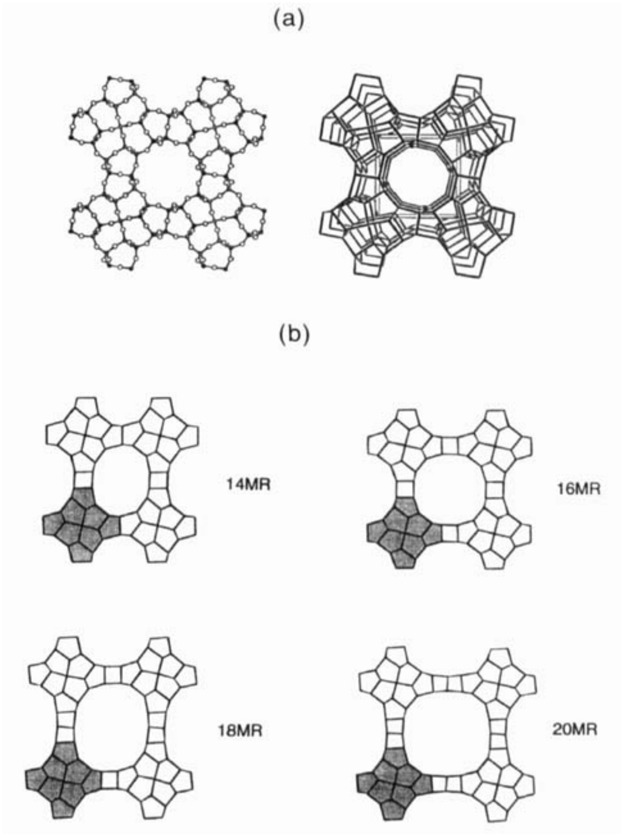

Figure 6. Schematic illustrations of a) the structure of VPI-8 and b) extra-large pore nets constructed from the "pinwheel" unit.

Clearly, there are numerous lines of thought to the preparation of extra-large pore materials. Here, I have outlined only a few.

Issues of Concern with Extra-Large Pore Materials: In spite of the great progress that has quickly been achieved in preparing extra-large pore materials since the announcement of VPI-5 in 1987, there remain numerous unresolved issues. The stability of UTD-1 provides reason to believe that extra-large pore materials will find practical application in the future. Although the issue of stability will not vanish, it is clearly being resolved. Below, I discuss issues of concern for the prepartion of extra-large pore materials.

One question that always arises is how large a pore size is possible? As before, I would argue that the extra-large ring size is not the cause of instability, but rather the stability is dictated by the stability of the units that build the structure. Thus, 24MR nets like those of Barrer and Villiger appear feasible from a structural point of view. However, it is not clear whether the organizational complexity of the synthesis medium must increase with increasing ring size. I will discuss two issues here that relate to the problems of synthesizing extra-large pore materials. First, it is unlikely that a molecular sieve material could be synthesized in water if the density of the crystal were to be less than that of water (for all practical concerns, water is the synthesis medium of choice). This is because the crystals thus formed would float to the surface upon nucleation and make the subsequent growth difficult (implies a nonviscous reaction medium). If no organic structure-directing agents are used, this is not an issue. If however, organic–inorganic composite structures are formed, then this issue becomes relevant. For example, by using a framework density of 2.5 $\mathrm{g\,cm^{-3}}$, water at 1 $\mathrm{g\,cm^{-3}}$, and an organic density of 0.6 $\mathrm{g\,cm^{-3}}$, the relation shown in Equation (1) can be formulated, where x is the void fraction of the crystal.

$$\underbrace{(2.5\,\mathrm{g\,cm^{-3}})(1-x)}_{\text{inorganic}} + \underbrace{x(0.6\,\mathrm{g\,cm^{-3}})}_{\text{organic}} \leq 1\,\mathrm{g\,cm^{-3}} \qquad (1)$$

Use of this approximation gives $x \leq 0.79$. Void fractions of known zeolites are all less than 0.5 and the void fractions of the 24MR structures fall below this predicted boundary. However, the correlation of Brunner and Meier suggests that 3MR-type frameworks could have void fractions in the range of 0.7–0.8. If this crude calculation provides an approximation to the bound on void volume, then it appears there is plenty of operating space for the synthesis of extra-large pore materials. Additionally, if the molecular sieve were to nucleate within a gel particle, then it may be trapped in the gel and not allowed to float to the surface. Thus, the bound on void volume may only apply to those preparations not involving thick gels. Second, if larger rings are to be constructed, can the organizational complexity that is expected to increase with increasing ring size when using uniform-sized building units be overcome by employing larger building units? The answer to this question is unclear because it remains unknown how these structures are assembled at the molecule level. Clearly, larger building units could lead to large rings (e.g., "pinwheel" units). Compare, for example, the β-cage in zeolite A with the α-cages that are in cloverite (see Figure 7). (Although these cages are most likely not the units that actually build the pore structures during the assembly process, they show how larger entities can construct larger pores.) If larger units can be forced to form, then it may be possible to dictate the creation of extra-large pores. It is known that tetramethylammonium (TMA) cations that form β-cages can be used in combinations with larger organics (e.g., tetrapropylammonium (TPA) cations) to form the large pore material SAPO-37 (TMA in β-cages and TPA in large cages[36]). Thus, structure-directing α-cages or even larger cages in conjunction with extra-large pore containing features by using two different organics appears feasible. Alternatively, instead of thinking about building structures from the assembly of small species, one can imagine the construction of three-dimensional structures from precursors that already have some degree of order. Schreyeck et al. showed that a two-dimensional (layered) material that had a high degree of structural order could be transformed into a zeolite of the ferrierite type.[37] The transformation from a layered to a three-dimensional structure appears to occur with other materials as well, for example, VPI-5,[38] MCM-22,[39] and ERB-1.[40] Therefore, another strategy for the preparation of extra-large pore materials could be through the use of a structured intermediate.

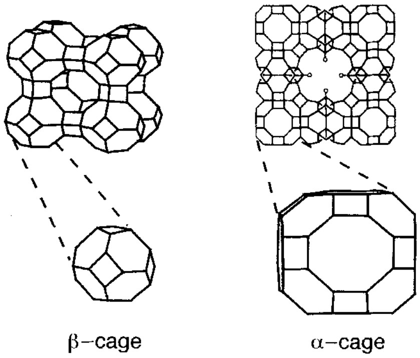

Figure 7. Schematic illustrations of the structures of zeolite A (left) and cloverite (right).

Summary

Although it has only been a decade since the discovery of VPI-5, the first extra-large pore material, the preparation of numerous other extra-large pore materials, including zeolites, has occurred. Additionally, the understanding of some of the issues germane to the preparation and use of crystalline solids with pore sizes above 10 Å is proceeding. Thus, it is likely that it is only a matter of time before commercial application of extra-large pore materials will appear. However, it is clear that although these types of molecular sieves could be useful in certain applications, they could be too large for others, as can be seen, for example, in the hydrocracking results of Santilli et al.[41] Therefore, judicious choices of reaction/separation applications will be necessary for successful commercialization.

Although great progress is currently being made in the quest for extra-large pore molecular sieves, there are numerous questions that remain. For example, a large body of work is emerging on the preparation of organic-based networks that possess extra-large rings (e.g., ref. [42]). Will these materials be able to function in a manner similar to the inorganic solids described here? Clearly, they will not be useful for high-temperature applications. However, they may find use and compete with the inorganic materials for low-temperature (and most probably liquid-phase) applications. Additionally, numerous hypothetical organic and inorganic networks have appeared, and it remains unclear why these materials, such as the 24 MR structures of Barrer and Villiger, have eluded synthesis thus far. Despite the fact that numerous unanswered questions remain, the field of extra-large pore materials is flourishing. The demand for these types of materials is increasing and will thus motivate expanded efforts in this area.

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Note added in proof: We recently prepared another 14 MR zeolite, CIT-5 (Wagner et al., *Chem. Commun.* **1997**, in press).