

News Item

Grand Openings for Cloverite

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Microporous crystalline solids comprise a class of materials whose main uses are as adsorbents, catalysts and ion exchangers. Zeolites, the best known of these, are built from tetrahedral units of SiO_4 and AlO_4 which connect to form crystalline structures with cavities and/or channels large enough to accommodate (or host) guest molecules. The degree of structural specificity achievable with molecular sieves is highly advantageous in the synthesis of materials with precise functions, such as optically active materials. Estermann *et al.* [1] report a new molecular sieve, which they call cloverite, which has a supercage of 30 Å diameter, significantly larger than any other known cage. Although it is cloverite's most notable feature, the supercage is only one of several structural aspects that may give the new material unusual catalytic properties.

Cloverite's chemical cousins, the phosphate-based molecular sieves (built from PO_4 and MO_4 tetrahedra where M can be Al, Ga, Zn, Be and so on), have been known for approximately a decade. Normally, these materials are made solely from tetrahedral units, as are zeolites. Therefore, one of the interesting features of cloverite is the presence of terminal hydroxyl groups (PO_3OH and GaO_3OH) which are an intimate part of the structure. (Because the framework does not fully consist of four connected tetrahedra it is called an interrupted framework.) The 20-membered ring pore of cloverite (the ring number specifies the number of phosphorus and metal atoms that form the ring) includes four terminal hydroxyl groups which intrude into the opening to give it a cloverleaf shape.

Zeolites with pores consisting of 12-membered rings have been known for many years. But it was only in 1988 that we reported [2] the first molecular sieve with larger pores, VPI-5. This is an aluminophosphate containing unidimensional, circular pores made of 18-membered rings with free diameters of about 13 Å. Thus, cloverite is unique both in that it has the largest ring size and in that it is the only molecular sieve to have a cloverleaf pore geometry. Although this geometry may exclude from the crystal interior of cloverite certain molecules taken up by VPI-5, the unusual shape may be useful in creating novel shape-induced adsorption properties.

The most exciting feature of cloverite is its 30-Å cage. Each cage can be accessed through six clover-shaped pores, making the material's pore system

three-dimensional; VPI-5, by contrast, is unidimensional. As described previously [3], multidimensional, large-pore molecular sieves have many advantages. Estermann *et al.* comment on several of cloverite's, so I will concentrate on a specific example – catalyst immobilization – of how cloverite could be used as a host.

Over the past decade or so, zeolites have been used for a kind of ship-in-a-bottle synthesis of organometallic complexes: the individual reagents are small enough to enter the pore system, but the assembled complexes are too large to escape the cages. Such complexes are often highly effective as catalysts, especially in the synthesis of chiral (asymmetric) compounds. The trapping, or immobilization, of the complexes is often desirable because of the expense of their constituent metals and intricate ligands. Until now, the 13-Å cages have limited the range of catalysts that may be immobilized, but cloverite's expanded, 30 Å cage should loosen that restriction. For example, chiral versions could be made in cloverite of the achiral rhodium phosphine complexes synthesized [4] in zeolite X and Y. Such complexes could be used to catalyze asymmetric reactions to form bioactive molecules such as L-DOPA.

Of course, biocatalysts are not the only interesting guests for cloverite. Quantum-sized semiconductor particles – particles so small that quantum-mechanical effects dominate their behaviour – are a new class of materials being closely studied. These could be controllably synthesized in the cages of cloverite as they have been in other microporous solids (see the *News and Views* article by Grätze [5]). And although the cage surfaces will not be so different in atomic-scale geometry from those of nonmicroporous catalysts, the combination of the unique pore shape and the large number of terminal hydroxyl groups may endow cloverite with unusual catalytic properties.

The synthetic route to cloverite holds the promise of interesting future possibilities. The use of fluoride (F^-) appears critical to the synthesis of cloverite, as it remains encapsulated within the material's paired 4-membered rings after the synthesis. Estermann *et al.* report that another gallophosphate with the zeolite A structure (LTA) was also synthesized using F^- . The LTA structure includes a large number of double 4-membered rings and numerous structures can be derived, in principle, using these structural units. So we can expect a plethora of new molecular sieves to follow (an equivalent explosion of activity followed the first synthesis of aluminophosphate molecular sieves).

The recent flourish of new molecular sieves with pore sizes greater than 12-membered rings (VPI-5, $AlPO_4$ (ref. 6) with 14-membered rings, and now cloverite) after years of stagnation at that limit, is probably attributable to the switch from the silica-based syntheses of zeolites and silicates to the phosphate-based structures [7]. The crystallization of the latter (from acidic reaction mixtures, as opposed to the basic ones of the zeolites and silicates) clearly proceeds in a different way to allow the formation of large rings. Estermann *et al.* comment that a pure silica form of an aluminophosphate (AST) molecular sieve which contains a large number of double 4-membered rings can be synthesized using F^- . Thus, they provide clues on how it may be possible to synthesize the first silica-based molecular sieve with pores consisting of greater than 12-membered rings. A silica

analogue of cloverite may in fact be a good candidate, as intracrystalline terminal silanol groups (SiO_3OH) have been observed in significant quantities in other essentially pure silica molecular sieves like ZSM-5.

References

1. M. Estermann, L. B. McCustar, C. Baerlocher, A. Merrouche, and H. Kessler: *Nature* **352**, 320–323 (1991).
2. M. E. Davis, C. Saldarriaga, C. Montes, J. Garces, and C. Crowder: *Nature* **331**, 698–699 (1988).
3. M. E. Davis: *Nature* **337**, 117 (1989).
4. B. E. Hanson *et al.*: *Inorg. Chem.* **23**, 52–56 (1984).
5. M. Grätzel: *Nature* **338**, 540–541 (1989).
6. R. M. Dessau *et al.*: *Zeolites* **10**, 522–524 (1990).
7. S. T. Wilson *et al.*: *J. Am. Chem. Soc.* **104**, 1146–1147 (1982).