Journal of Inclusion Phenomena **6** (1988), 547–548.

News Item

New Family of Molecular Sieves Developed*

A new family of molecular sieves has been developed at Virgina Polytechnic Institute & State University, Blacksburg, in collaboration with Dow Chemical. Based on aluminophosphates, the new sieves have unusually large pores and the ability to host a variety of adatoms – atoms that are added in, usually for catalytic use.

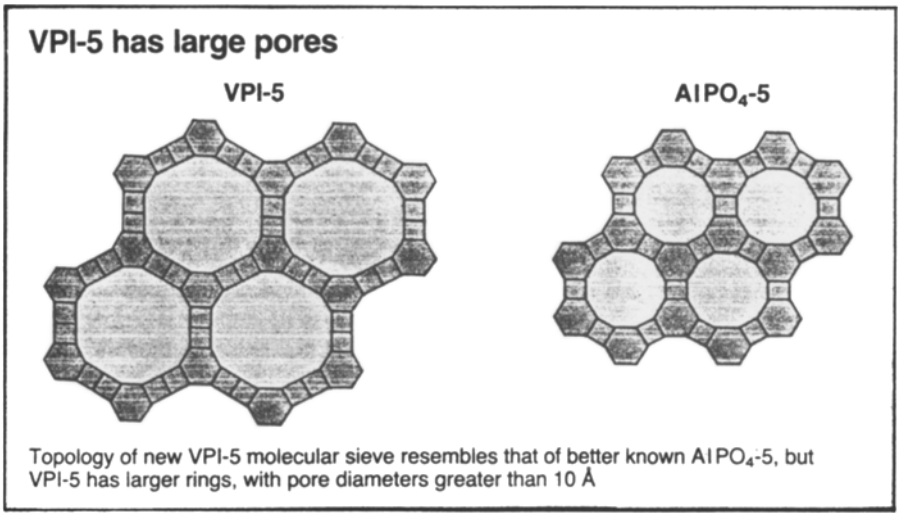
The history of molecular sieves can be traced back to 1756. The most well-known and widely used sieves are the natural and synthetic zeolites – namely, aluminosilicates. They are widely used as industrial catalysts and drying agents, and for a number of compounding applications. At present, the best-known zeolite is probably Mobil's ZSM-5, a synthetic material used to produce gasoline and other motor fuels from methanol, produce lower olefins from methanol, and upgrade certain naphthas. The most recent addition to the roster of molecular sieves has been the aluminophosphates (alpos), which have a cage and channel structure similar to zeolites but have different pore dimensions. Pure silica analogs of some of the zeolites and at least one aluminophosphate also have been synthesized.

The zeolites, some silica polymorphs, and the alpos are all composed of tetrahedrally coordinated atoms (T-atoms), with the silicon, aluminum, phosphorus, and other atoms connected to adjacent atoms by atomic bridges. Until the discovery of the new sieves by chemical engineering professor Mark E. Davis and coworkers at VPI, the largest rings in natural and synthetic molecular sieves consisted of 12 T-atoms with a free pore diameter available for adsorption of about 10 Å. Other crystalline systems are known with greater pore diameters, but they are not of commercial use as petrochemical catalysts.

Davis and his associates have synthesized molecular sieves with pores larger than 10 Å in diameter. Collectively called VPI-5, they are aluminophosphate-based sieves with 18-membered rings of T-atoms in the same general 3D topology as the more familiar alpos. The framework density of the VPI-5 series is 12.7 T-atoms per 1000 cubic Å.

The VPI-5 materials are made from a reactive aluminophosphate gel, which contains a structure directing agent (template). It has not been possible to produce the sieves without the agent. From neutron activation analyses, the aluminum-to-phosphorus ratio is known to be about 1. The new molecular sieves have been heated above 800°C without any evidence of phase transition. The symmetry is hexagonal, with unit cell dimensions where a equals 18.989 Å and c equals 8.112 Å.

Davis compares the relative topology of VPI-5 with that of the more familiar alpo $AlPO_4$-5. The topology of VPI can be generated by inserting a four-membered ring adjacent to each four-membered ring in $AlPO_4$.



Davis and his group at VPI have synthesized a growing family of molecular sieves based on VPI-5. These contain a variety of adatoms including silicon and cobalt. At present, work is continuing on the confirmation of framework location for these elements. The total pore volume of VPI-5 is very large. When determined with water adsorbate, the fraction is 0.5 cc water per g of solid. All other adsorbates have access only to the large pore system and not to any of the smaller pores. Sorption of oxygen and of nitrogen are nearly the same at about 0.25 cc per g, whereas the adsorption of organics is fairly consistent in the range of 0.15 to 0.19 cc per g.

Of particular interest is the adsorption of triisopropylbenzene, which readily adsorbs in VPI-5 and reaches equilibrium in several minutes. Using water and triisopropylbenzene as pycnometer fluids in VPI-5, the respective densities were determined as 2.56 and 1.64 g per cc. Assuming the total volume of VPI-5 is represented by the water data and that triisopropylbenzene equilibrates only in the large pores, the large pore volume can be estimated at 0.164 cc per g. The kinetic diameter of triisopropylbenzene is 8.5 Å. This is the largest molecule used as an adsorbate thus far, but there is still room for even larger molecules.

There is some interest in possible use of VPI-5 sieves in pharmaceutical applications for purification of large molecules. But the chief commercial applications would probably be in petroleum refining for cracking very large molecules to increase the motor fuel yields from bottom-of-the-barrel residua.

Davis' principal collaborator at Dow was researcher Juan Garces. Dow and the National Science Foundation supported the work through a Presidential Young Investigator Award to Davis. Garces notes that the Davis-Garces discovery marks a practical example of industry-academic cooperation at a time of increasing criticism of industry for failing to adequately support academic research and researchers. In the course of the discovery, the unique facilities at both Dow and VPI were utilized, he says. Garces notes that of particular merit was the work of Dow's Cyrus Crowder, who made many of the structural determinations for the new molecular sieves.

Chicago JOSEPH HAGGIN