

New Family of Molecular Sieves Synthesized

Replacement of silicon with phosphorus in zeolites provides novel structures and unexpected properties

A new family of molecular sieves with some unusual and potentially useful properties was reported at the recent American Chemical Society (ACS) meeting* by a team from the Union Carbide Corporation Technical Center in Tarrytown, New York. The new materials are aluminophosphates in contrast to the conventional aluminosilicates, and most of them have previously unknown structures. The report was presented by Stephen T. Wilson; other members of the team included Brent M. Lok, Celeste A. Messina, Thomas R. Cannan, and Edith M. Flanigen.

Zeolites were first commercialized in 1954 by Union Carbide. Their unusual structures feature a crystalline framework of aluminate and silicate moieties surrounding voids that vary in size from 0.3 to 0.8 nanometer in diameter. The presence of the void, combined with anionic binding sites, confers on the materials useful properties that have given rise to more than 10,000 patents and an annual output that now exceeds 325 million pounds. Their uses include removing water from organic liquids and gases, separation of organic molecules of specific shapes and sizes, and catalysis of organic reactions. They are also used as "builders" to replace phosphates in detergents, an application that now accounts for more than 75 percent of consumption.

*184th National Meeting, 12 to 17 September, Kansas City, Missouri.

The trend in zeolite chemistry in recent years, Flanigen says, has been reduction of the amount of aluminum in the molecular sieves. The first zeolites had a 1:1 ratio of silicon to aluminum, but that ratio has grown progressively higher in recent years. The Union Carbide group has reversed this trend by removing all of the silicon and replacing it with phosphorus.

The new molecular sieves have a formula of $\text{Al}_2\text{O}_3 \cdot (1.0 \pm 0.2)\text{P}_2\text{O}_5$ or, more generally, AlPO_4 . They are prepared by combining the two components in water and crystallizing at temperatures ranging from 100° to 250°C. Amines and quaternary ammonium ions are used as templates; the aluminophosphates crystallize in characteristic shapes around the amines. Some of the amines that are used include tripropylamine, methylpyridine, choline, triethanolamine, and tetraethylammonium hydroxide. Many zeolites are prepared in the same manner, but most of these are prepared with alkali metal salts of quaternary ammonium ions. In contrast, Wilson says, more than 80 percent of the aluminophosphates can be prepared with free amines.

After crystallization, the molecular sieves are calcined at 600° to 1000°C to destroy the amines, thereby forming the characteristic voids. The new materials have been produced in the entire range of pore volumes and sizes characteristic of conventional zeolites. They have also

been produced with at least 20 different three-dimensional framework structures; of these 14 are microporous and six are two-dimensional, layer-type materials. Most of these structures are novel, but three are structurally related to zeolites.

The aluminophosphates have many properties that differ from those of the zeolites. Perhaps most important, they are electrically neutral, since the aluminum and phosphate charges cancel each other. They thus have no accompanying cations and no potential use as ion exchange materials or detergent builders. Because of this absence of charge, the Union Carbide scientists expected the aluminophosphates to be hydrophobic like the pure silicate zeolites, which also are electrically neutral.

They were surprised to find that the new materials are moderately hydrophilic, perhaps, they think, because the difference in electronegativity between aluminum and phosphate creates a dipole moment that attracts the dipole of water molecules. Preliminary laboratory studies suggest that the hydrophilicity is strong enough for the molecular sieves to be used successfully as drying agents, but sufficiently weak for regeneration of the agent not to require a large amount of energy, as is the case with conventional aluminosilicate molecular sieves.

Some zeolites are also highly acidic, a fact that is important in most petrochemical catalytic reactions. The aluminophosphates are much less acidic, which suggests that they could be used where less extensive structural changes are desired. The Union Carbide group is now screening a number of potential catalytic applications, but they are not yet prepared to disclose any of them. They will, however, make samples available to other investigators in 1983.

So far, only one of the new materials, termed AIPO-5, has been completely characterized. J. Michael Bennett of Union Carbide reported that AIPO-5 is formed around a template of tetrapropylammonium hydroxide, which assumes the form of a tripod with tucked-in feet. The zeolite itself is formed from crown-shaped rings of 12 alternating aluminum- and phosphorus-oxygen tetrahedra; these are extended in the third dimension to produce a channel in which all the dipoles are oriented in the same direction.—THOMAS H. MAUGH II

From Biomass to Gasoline

Zeolites are widely used as catalysts in the petroleum and petrochemical industries, particularly for cracking petroleum. One recent new use, developed at Mobil Research and Development Corporation, is a process that converts methanol to high-octane gasoline in one step. At the ACS meeting, Martin Chang of Purdue University reported the development of a modification of this process that can, in one step, produce gasoline from ethanol derived from the fermentation of biomass.

The key, Chang says, was finding an optimum mixture of water and ethanol; he uses a broth of 72 percent ethanol and 28 percent water. The methanol conversion, in contrast, is anhydrous. The catalyst strips the elements of water from the ethanol and combines the carbon fragments into larger molecules. Chang estimates the cost of the process at \$1.26 per gallon, but suggests that the process is more efficient than using ethanol as a fuel because distillation of water from the ethanol for such a use requires a large amount of energy.—T.H.M.