# New Molecular Sieve Materials : Aluminophosphates and Silicoaluminophosphates

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The most widely known molecular sieves are the aluminosilicate zeolites. Structurally, zeolites are based on infinitely extending, three-dimensional networks of $AlO_4$ and $SiO_4$ tetrahedra linked by the sharing of oxygen atoms [1]. The structural formula of a crystallographic unit cell of a zeolite may be expressed in terms of the oxides as follows:

$$M_{x/n} [ (AlO_2)_x (SiO_2)_y ] \cdot wH_2O.$$

Here M is a cation of valence n, w is the number of water molecules, and the sum of x and y is the total number of tetrahedra in the unit cell.

The zeolites that have received the most scientific study and have generated the most industrial interest as adsorbents and catalysts are relatively few in number [2]. The structures of principal interest in hydrocarbon conversion catalysis are the large-pore zeolites, type X, type Y and mordenite. More recently the smaller pore structures, type A and ZSM-5 have been of interest in shape selective catalysis [2b].

The most common use of molecular sieves is in petroleum cracking and reforming. However, many hydrocarbon molecules contained in petroleum are too big to fit into the pores of the sieves. The largest rings in natural occurring zeolites and synthetic molecule sieves contain only 12-membered tetrahedral rings with free diameter available for adsorption being of the order of about 10 Å [2a]. It is the extension to higher than 12 membered ring pores in zeolitic compounds that has been the focus of recent work on new porous molecular sieves.

Several new classes of molecular sieves have recently been reported including aluminophosphates ($AlPO_4$) and silicoaluminophosphates (SAPO). These microporous solids exhibit properties characteristic of zeolites but show different physicochemical traits. These new compounds show promise in increasing the ring size from 12-membered to higher forms.

Aluminophosphate materials are synthesized hydrothermally at 100-250°C [3]. Twenty, three-dimensional $ALPO_4$ framework structures are known, of which 14 are microporous and 6 are two-dimensional layer type materials. Most of the three-dimensional structures are novel. However, three are structurally related to the zeolite family, with framework topologies of the erionite/offretite type ($ALPO_4$-17), the sodalite type ($ALPO_4$-20), and the analcime type ($ALPO_4$-24). They have a formula, in terms of mole ratios of oxides of

$$xR\ Al_2O_3\ (1.0 \pm 0.2)\ P_2O_5 \cdot yH_2O,$$

where R is an essential template such as an organic amine.

The other new microporous materials, the silicoaluminophosphates, are also synthesized hydrothermally in the presence of organic amine templates (denotes R) [4]. This class encompasses thirteen, three-dimensional framework oxide structures including structural analogues of the zeolites, $AlPO_4$ as well as the novel structures. The sieves have the general composition in the anhydrous form of

$$wR\ (Si_xAl_yP_z)\ O_2$$

where x+y+z=1.

The results of NMR and FTIR investigations of $AlPO_4$-5, $AlPO_4$-17, SAPO-5 and SAPO-37 lead to the following conclusions [5]. First, the $^{27}Al$ and $^{31}P$ NMR spectra are in accordance with a structure of alternating $[AlO_4]$ and $[PO_4]$ tetrahedra. Second, water interacts with the framework of $AlPO_4$ to produce a cross-polarizable octahedral type chemical shift in the $AlPO_4$-17 sieve. Third, the $^{29}Si$ NMR spectra are consistent with tetrahedral $Si(OAl)_4$ structures and provide information regarding the method of substitution of the silicon atoms into the aluminophosphate lattice. Finally, both Brönsted and Lewis acid sites are present in the SAPO sieves, as shown by the IR experiments involving the adsorption of pyridine.

The first molecular sieve having a pore greater than 12 membered ring was prepared in 1987 [6a]. Denoted as VPI-5, this molecular sieve is a new member of $AlPO_4$ materials. The large pores of the VPI-5 material are long channels circumscribed by rings containing eighteen tetrahedral units and possess free diameters of about 12-13 A [6b]. This recent discovery suggests that it could be possible to extend the pore size of the molecular sieves infinitely [6c].

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