

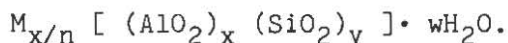
New Molecular Sieve Materials : Aluminophosphates
and Silicoaluminophosphates

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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:



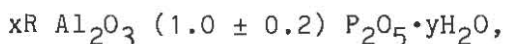
Here M is a cation of valence n, w is the number of water molecules, and the sum of x and y is the total number of tetrahedra in the unit cell.

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.

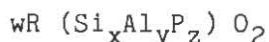
Aluminophosphate materials are synthesized hydrothermally at 100-250°C [3]. Twenty, three-dimensional $AlPO_4$ framework structures are known, of which 14 are microporous and 6 are two-dimensional layer type materials. Most of the three-dimensional structures are novel. However, three are structurally 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



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



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 $[\text{AlO}_4]$ and $[\text{PO}_4]$ 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 $\text{Si}(\text{OAl})_4$ 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 Å [6b]. This recent discovery suggests that it could be possible to extend the pore size of the molecular sieves infinitely [6c].

References

1. General references:
 - (a) Breck, D. W., "Zeolite Molecular Sieves," Wiley Interscience: New York, 1974.
 - (b) Bolten, A. P., "Experimental Methods in Catalytic Research II," Academic Press: New York, 1976, 1.
2.
 - (a) Breck, D. W.; Anderson, R. A., "Kirk-Othmer Encyclopedia of Chemical Technology," John Wiley & Sons: New York, 1981, 638.
 - (b) Barrer, R. M., "Hydrothermal Chemistry of Zeolites," Academic Press: London, 1982.
 - (c) Barrer, R. M., "Porous Crystals: A Perspective," Stud. Surf. Sci. Catal. 1986, 28, 1.
3.
 - (a) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigan, E. M., "Aluminophosphates Molecular Sieves: A New Class of Microporous Crystalline Inorganic Solids," J. Am. Chem. Soc. 1982, 104, 1146.
 - (b) Bennett, J. M.; Cohen, J. P.; Flanigan, E. M.; Pluth, J. J.; Smith, J. V., "Crystal Structure of Tetrapropylammonium Hydroxide-Aluminophosphate Number 5," Am. Chem. Soc. Symp. Ser. 1983, 218, 109.
 - (c) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigan, E. M., "Aluminophosphate Molecular Sieves," Am. Chem. Soc. Symp. Ser. 1983, 218, 79.
 - (d) Wilson, S. T.; Lok, B. M.; Flanigan, E. M., "Synthesis of AlPO_4 Molecular Sieves," Proceedings, 6th International Zeolite Conference, Reno, 1983, 97.

- (e) Pyke, D. R.; Whitney, P.; Houghton, H., "Chemical Modification of Crystalline Microporous Aluminum Phosphates," Appl. Catal. 1985, 18, 173.
- (f) Louse, U.; Noack, M.; Jahn, E., "Adsorption Properties of the $AlPO_4-5$ Molecular Sieve," Adsorp. Sci. Tech. 1986, 3, 19.
- (g) Qinhuo, X.; Jialu, D.; Aizhen, Y.; Changtai, J., "Synthesis and Properties of Several Aluminophosphate Molecular Sieves," Proceedings, International Symposium on Zeolite Catalysis, Siófok, Hungary, 1985, 99.
4. (a) Lok, B. M.; Messina, C. A.; Patton, R. L.; Gajek, R. T.; Cannon, T. R.; Flanigan, E. M., "Silicoaluminophosphate Molecular Sieves: Another New Class of Microporous Crystalline Inorganic Solids," J. Am. Chem. Soc. 1984, 106, 6092.
- (b) Qinhuo, X.; Aizhen, Y.; Schulin, B.; Kaijin, X., "Catalytic and Acidic Properties of SAPO-5 Molecular Sieve," Stud. Surf. Sci. Catal. 1986, 28, 835.
- (c) Pellet, R. J.; Long, G. N.; Rabo, J. A., "Molecular Sieve Effects in Carboniogenic Reactions Catalyzed by Silicoaluminophosphate Molecular Sieves," Stud. Sci. Catal. 1986, 28, 843.
5. (a) Blackwell, C. S.; Patton, R. L., "Aluminum-27 and Phosphorus-31 Nuclear Magnetic Resonance Studies of Aluminophosphate Molecular Sieves," J. Phys. Chem. 1984, 88, 6235.
- (b) Müller, D.; Fahlke, J. B.; Ladwig, G.; Haubenreisser, U., "High Resolution ^{27}Al and ^{31}P n.m.r. Studies of the Aluminum Phosphate Molecular Sieve $AlPO_4-5$," Zeolites 1985, 5, 53.
- (c) Appleyard, I. P.; Harris, R. K.; Fitch, F. R., "Aluminum-27, Phosphorus-31, and Silicon-29 MAS NMR Studies of the Silicoaluminophosphate Molecular Sieve SAPO-5," Chem. Lett. 1985, 1747.
- (d) Gelsthorpe, M. R.; Theocharis, C. R., "The Efficient Removal of Organic Templating Molecules from Aluminophosphate Molecular Sieves," J. Chem. Soc., Chem. Commun. 1986, 781.
- (e) Bennett, J. M.; Dytrych, W. J.; Pluth, J. J.; Richardson, Jr., J. W.; Smith, J. V., "Structural Features of Aluminophosphate Materials with $Al/P=1$," Zeolites 1986, 6, 349.
- (f) Saldarriaga, L. S.; Saldarriaga, C.; Davis, M. E., "Investigations into the Nature of a Silicoaluminophosphate with the Faujasite Structure," J. Am. Chem. Soc. 1987, 109, 2686.
6. (a) Bishop, J. E., "Why a New Sieve is Exciting the Oil, Chemical Industries," The Wall Street J. Sep. 18, 1987.
- (b) Davis, M. E.; Saldarriaga, C.; Montes, C.; Garces, J.; Crowder, C., "VIP-5: The First Molecular Sieve with Eighteen Membered Rings," Nature, in press.
- (c) Smith, J. V.; Dytrych, W. J., "Nets with Channels of Unlimited Diameter," Nature 1984, 309, 607.