

## Aluminophosphate molecular sieves and the periodic table

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**Abstract** - New generations of crystalline microporous molecular sieve oxides have been discovered based on the novel aluminophosphate family by incorporating one or more of an additional thirteen elements from the Periodic Table into the  $AlPO_4$  framework. Elements incorporated include Li, Be, B, Mg, Si, Ga, Ge, As, Ti, Mn, Fe, Co, and Zn, spanning monovalent through pentavalent framework cationic species. The new materials comprise more than two dozen structures and two hundred compositions, including multi-element frameworks containing combinations of up to six framework cations. Pore sizes range from 0.3nm to 0.8nm encompassing small, intermediate and large pore structures. The new molecular sieves are synthesized by hydrothermal crystallization of reactive aluminophosphate gels containing the additional framework elements and an organic template. Proof of framework incorporation includes the formation of novel structures, the enhancement of catalytic activity, elemental analysis, and various spectroscopic evidence. The Bronsted acidity observed ranges from weakly to strongly acidic. This landmark discovery of new generations of molecular sieve materials represents a remarkable diversity in crystal structure and crystal chemistry, and offers a nearly unlimited number of design parameters to tailor adsorptive and catalytic properties.

### INTRODUCTION

Historically, molecular sieves have been a materials-driven science and technology. The initial discovery of some twenty synthetic aluminosilicate zeolites in the late 1940's and early 1950's by Breck et al (ref. 1a) at the Union Carbide Laboratories served as the beginning of today's large molecular sieve industry. The early synthetic zeolites A and X discovered by Milton (ref. 1b) were aluminum-rich, and were the first introduced commercially for adsorptive and catalytic applications. During the 50's and early 60's more siliceous zeolite frameworks were reported and commercialized such as zeolite Y (Breck ref. 2) and the large pore mordenite "Zeolon" (Sand ref. 3). In the late 1960's and early 1970's the high silica zeolites, such as the zeolites Beta and ZSM-5, were reported by Wadlinger et al (ref. 4) and Argauer et al (ref. 5) from the Mobil Research and Development Laboratories. The successive incorporation of even higher concentrations of silicon and the elimination of aluminum in the framework led to the silica molecular sieves, as typified by silicalite (ref. 6).

In the late 1970's the Union Carbide Laboratories set out to discover a new generation of molecular sieves. The strategy was to explore new framework compositions of oxides outside of the then-known aluminosilicate zeolites and silica molecular sieves. The Periodic Table was viewed as the potential scope for new framework compositions and structures. Based on crystal chemical principles and the known crystal chemistry of framework oxides, the first elements explored as the tetrahedral framework cations were aluminum and phosphorus. Initial success resulted in the discovery of the aluminophosphate ( $AlPO_4$ ) molecular sieves reported in 1982 by Wilson et al (ref. 7). The addition of silicon to the aluminum and phosphorus framework elements resulted in the silicoaluminophosphate (SAPO) molecular sieves reported by Lok et al (ref. 8) in 1984. The metal aluminophosphate (MeAPO) molecular sieves with frameworks containing aluminum, phosphorus and metal cations (Me), where  $Me = Mg^{2+}, Mn^{2+}, Fe^{2+,3+}, Co^{2+}$  and  $Zn^{2+}$ , were reported by Messina et al (ref. 9) and Wilson et al (ref. 10) in 1985 and 1986.

The remarkable success of the Periodic Table strategy will be described in this paper. We now report incorporation of thirteen elements from the Periodic Table into aluminophosphate

frameworks, Li, Be, B, Mg, Si, Ti, Mn, Fe, Co, Zn, Ga, Ge, and As. The resulting new generations of crystalline microporous molecular sieve oxides comprise more than two dozen structures and two hundred compositions. A detailed and comprehensive discussion of such a large number of materials is beyond the scope of this paper. We will attempt here to give an overview of selected structures and compositions.

## NOMENCLATURE

The materials are classified into binary (2), ternary (3), quaternary (4), quinary (5), and senary (6) compositions based on the number of elements contained in the cationic framework sites of any given structure. A normalized  $\text{TO}_2$  formula represents the relative concentration of framework elements in the composition,  $(\text{E}_x\text{Al}_y\text{P}_z)\text{O}_2$ , where E1 is the incorporated element and x, y and z are the mole fractions of the respective elements in the composition. Acronyms describing the framework composition are shown in Table 1, e.g., SAPO =  $(\text{Si},\text{Al},\text{P})\text{O}_2$  composition. The structure type is indicated by an integer following the compositional acronym, e.g., SAPO-5 is a  $(\text{Si},\text{Al},\text{P})\text{O}_2$  composition with the type 5 structure. The numbering of the structure type is arbitrary and bears no relationship to structural numbers used previously in the literature, e.g. ZSM-5, and only identifies structures found in the aluminophosphate-based molecular sieves. The same structure number is used for a common structure type with varying framework composition.

TABLE 1. Acronyms for Framework Compositions

| $\text{TO}_2$ , T= | Acronym | $\text{TO}_2$ , T= | Acronym | $\text{TO}_2$ , T= | Acronym |
|--------------------|---------|--------------------|---------|--------------------|---------|
| Si,Al,P            | SAPO    | Me,Al,P,Si         | MeAPSO  | Other Elements:    |         |
|                    |         | Fe,Al,P,Si         | FAPSO   | El,Al,P            | ElAPO   |
| Me,Al,P            | MeAPO   | Mg,Al,P,Si         | MAPSO   | El,Al,P,Si         | ElAPSO  |
| Fe,Al,P            | FAPO    | Mn,Al,P,Si         | MnAPSO  |                    |         |
| Mg,Al,P            | MAPO    | Co,Al,P,Si         | CoAPSO  |                    |         |
| Mn,Al,P            | MnAPO   | Zn,Al,P,Si         | ZAPSO   |                    |         |
| Co,Al,P            | CoAPO   |                    |         |                    |         |
| Zn,Al,P            | ZAPO    |                    |         |                    |         |

## RESULTS AND DISCUSSION

### Structures

The major structures crystallized in the new generations of  $\text{AlPO}_4$ -based molecular sieves are shown in Table 2. They include fifteen novel structures as well as seven

TABLE 2. Typical Structures in  $\text{AlPO}_4$ -Based Molecular Sieves

| Species                  | Structure Type | Pore Size, nm | Saturation $\text{H}_2\text{O}$ Pore Vol, $\text{cm}^3\text{g}^{-1}$ | Species                   | Structure Type | Pore Size, nm | Saturation $\text{H}_2\text{O}$ Pore Vol, $\text{cm}^3\text{g}^{-1}$ |
|--------------------------|----------------|---------------|--|---------------------------|----------------|---------------|--|
| <b>Large Pore</b>        |                |               |  | <b>Small Pore (cont.)</b> |                |               |  |
| 5                        | Novel, detm.   | 0.8           | 0.31   | 33                        | Novel          | 0.4           | 0.23   |
| 36                       | Novel          | 0.8           | 0.31   | 34                        | Chabazite      | 0.43          | 0.3  |
| 37                       | Faujasite      | 0.8           | 0.35   | 35                        | Levynite       | 0.43          | 0.3  |
| 40                       | Novel          | 0.7           | 0.33   | 39                        | Novel          | 0.4           | 0.23   |
| 46                       | Novel, detm.   | 0.7           | 0.28   | 42                        | Linde Type A   | 0.43          | 0.3  |
| <b>Intermediate Pore</b> |                |               |  | 43                        | Gismondine     | 0.43          | 0.3  |
| 11                       | Novel, detm.   | 0.6           | 0.16   | 44                        | Chabazite-like | 0.43          | 0.34   |
| 31                       | Novel          | 0.65          | 0.17   | 47                        | Chabazite-like | 0.43          | 0.3  |
| 41                       | Novel          | 0.6           | 0.22   |                           |                |               |  |
| <b>Small Pore</b>        |                |               |  | <b>Very Small Pore</b>    |                |               |  |
| 14                       | Novel, detm.   | 0.4           | 0.19   | 16                        | Novel          | 0.3           | 0.3  |
| 17                       | Erionite       | 0.43          | 0.28   | 20                        | Sodalite       | 0.3           | 0.24   |
| 18                       | Novel          | 0.43          | 0.35   | 25                        | Novel          | 0.3           | 0.17   |
| 26                       | Novel          | 0.43          | 0.23   | 28                        | Novel          | 0.3           | 0.21   |

structures with framework topologies related to those found in the zeolites, chabazite (34, 44, 47), erionite (17), gismondine (43), levynite (35), Linde Type A (42), faujasite (37), and sodalite (20). Also shown is the pore size and pore volume for each structure type. Pore volumes and pore sizes were determined by standard gravimetric adsorption techniques on samples calcined at 773–873K to remove the organic template and H<sub>2</sub>O. Pore size values result from the adsorption of "plug gauge" molecules of known kinetic diameter (ref. 11). The structures include large pore (0.7–0.8nm), intermediate pore (0.6nm), small pore (0.4nm), and very small pore (0.3nm) materials. Saturation water pore volumes vary from 0.16 to 0.35 cm<sup>3</sup>g<sup>-1</sup> comparable to the pore volume range observed in zeolites.

The novel structures which have been determined include types 5 (ref. 12), 11 (ref. 13), 14 (ref. 14), and 46 (ref. 15). The structure of AlPO<sub>4</sub>-5 (Figure 1) is hexagonal, a=1.373nm, c=0.848nm, and consists of columns of twisted 4- and 6-rings parallel to the c-axis outlining a unidimensional cylindrical channel bounded by 12-rings with a free diameter of 0.8nm. The related structure of AlPO<sub>4</sub>-11 (Figure 1), orthorhombic, a=1.35nm, b=1.87nm, c=0.845nm, is generated by removal of one-third of the 4-rings from the AlPO<sub>4</sub>-5 structure with concomitant conversion of each 12-ring channel into an elliptical 10-ring channel with a free crystallographic diameter of 0.67nm by 0.40nm. The 4- and 6-ring columns and the unidimensional channel are parallel to the c-axis. The templates incorporated into the channel during synthesis are also illustrated in Figure 1. The tetrapropylammonium template forming the AlPO<sub>4</sub>-5 structure and the di-n-propylamine template forming the AlPO<sub>4</sub>-11 structure are both sited in the channels with a stoichiometry of one per c-distance, providing a neat space-filling of the channel voids.

Present structural information and the observed Al and P stoichiometry (Al/P=1) indicate a strict alternation of Al and P tetrahedra in the AlPO<sub>4</sub> molecular sieve structures (ref. 16), and the absence of Al–O–Al, Si–O–P and P–O–P bonds in the AlPO<sub>4</sub>-based frameworks.

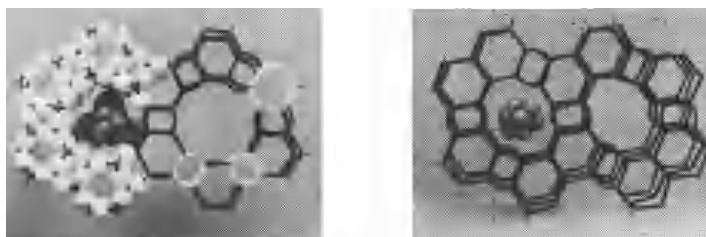


Fig. 1. Framework models of AlPO<sub>4</sub>-5 with Tetrapropylammonium (left), and AlPO<sub>4</sub>-11 with di-n-propylamine (right). View down the c-axis.

### Compositions

A summary of typical compositions and structures crystallized in the AlPO<sub>4</sub>, SAPO, MeAPO and MeAPSO families of compositions is shown in Table 3, and in the ELAPO and ELAPSO families in Table 4. An overview of the compositions, structures and properties of each is presented.

**AlPO<sub>4</sub>.** The AlPO<sub>4</sub> molecular sieves, the parent of the AlPO<sub>4</sub>-based families described here, exhibit an invariant framework composition with an Al/P ratio of 1 and a wide structural diversity. Thirteen microporous AlPO<sub>4</sub> structures have been reported including structures with the same framework topologies as zeolites, 17 (erionite) and 20 (sodalite), and novel structures, 5, 11, 14, 16, 18, 31 and 33. Their product composition expressed as an oxide formula, is xR·Al<sub>2</sub>O<sub>3</sub>·1.0±0.2P<sub>2</sub>O<sub>5</sub>·yH<sub>2</sub>O, where R is an amine or quaternary ammonium template, and x and y represent the amounts needed to fill the microporous voids. Calcination at a typical temperature of 773–873K removes the R and H<sub>2</sub>O and yields the microporous molecular sieve framework expressed as AlPO<sub>4</sub> or a TO<sub>2</sub> formula of (Al<sub>0.50</sub>P<sub>0.50</sub>)O<sub>2</sub>. The AlPO<sub>4</sub>'s exhibit excellent thermal and hydrothermal stability comparable to that observed with the more stable zeolites.

Their surface selectivity is mildly hydrophilic. Adsorption isotherms for O<sub>2</sub> and hydrocarbon adsorbates are essentially Type I, typical of micropore filling. Water isotherm shapes vary from Type I to Type V, depending upon structure. Adsorption pore volumes vary from 0.04 to 0.35 cm<sup>3</sup>g<sup>-1</sup>, and pore sizes from 0.3nm to 0.8nm, properties comparable to the range observed in zeolites.

The AlPO<sub>4</sub> frameworks are neutral and thus have nil ion exchange capacity. They exhibit weakly acidic catalytic properties. Their synthesis, properties and structures have been reported in detail elsewhere (ref. 7, 12, 14, 15, 16, 17).

**Silicoaluminophosphates (SAPO).** The next family of new molecular sieves are the silicoaluminophosphates (SAPO). They exhibit both structural diversity and compositional variation. Thirteen three-dimensional microporous structures have been reported, including the novel 40 and 41, and structures topologically related to: zeolites, 34 and 44 (chabazite), 35 (levynite), 37 (faujasite) and 42 (Linde Type A); the aluminophosphates, 5, 11, 16 and 31; and those found in both zeolites and

TABLE 3. Selected Structures and Compositions in Binary, Ternary and Quaternary Systems<sup>a</sup>

| Structure Type           | AlPO <sub>4</sub> | SAPO | MeAPO | (Me Elements)        | MeAPSO | (Me Elements)        |
|--------------------------|-------------------|------|-------|----------------------|--------|----------------------|
| <b>Large Pore</b>        |                   |      |       |                      |        |                      |
| 5                        | X                 | X    | X     | (Co, Fe, Mg, Mn, Zn) | X      | (Co, Fe, Mg, Mn, Zn) |
| 36                       | -                 | -    | X     | (Co, Mg, Mn, Zn)     | X      | (Co, Mg, Mn, Zn)     |
| 37                       | -                 | X    | -     |                      | -      |                      |
| 40                       | -                 | X    | -     |                      | -      |                      |
| 46                       | -                 | -    | -     |                      | X      | (Co, Fe, Mg, Mn, Zn) |
| <b>Intermediate Pore</b> |                   |      |       |                      |        |                      |
| 11                       | X                 | X    | X     | (Co, Fe, Mg, Mn, Zn) | X      | (Co, Fe, Mg, Mn, Zn) |
| 31                       | X                 | X    | -     |                      | X      | (Co, Fe, Mg, Mn, Zn) |
| 41                       | -                 | X    | -     |                      | -      |                      |
| <b>Small Pore</b>        |                   |      |       |                      |        |                      |
| 14                       | X                 | -    | X     | (Mg, Zn)             | -      |                      |
| 17                       | X                 | X    | X     | (Co, Fe, Mg)         | X      | (Co)                 |
| 34                       | -                 | X    | X     | (Co, Fe, Mg, Mn, Zn) | X      | (Co, Fe, Mg, Mn, Zn) |
| 44                       | -                 | X    | X     | (Co, Mg, Mn, Zn)     | X      | (Co, Fe, Mg, Mn, Zn) |
| 47                       | -                 | -    | X     | (Co, Mg, Mn, Zn)     | X      | (Co, Mg, Mn, Zn)     |
| <b>Very Small Pore</b>   |                   |      |       |                      |        |                      |
| 20                       | X                 | X    | X     | (Mg)                 | X      | (Co, Fe, Mg, Mn, Zn) |

<sup>a</sup>For elements Al, P, Si, Co, Fe, Mg, Mn and Zn. The X designation indicates compositions and structures observed in high purity and which are well characterized.

TABLE 4. Selected ELAPO and ELAPSO Structures and Compositions

| Structure Type           | Compositional Systems |                           |
|--------------------------|-----------------------|---------------------------|
|                          | ELAPO,<br>Elements    | ELAPSO,<br>Elements       |
| <b>Large Pore</b>        |                       |                           |
| 5                        | Be, Ga, Ge, Li, Ti    | Be, Ga, Ti                |
| 36                       | Be, Ga                | -                         |
| <b>Intermediate Pore</b> |                       |                           |
| 11                       | As, Be, Ti            | As, Ge, Ti                |
| 41                       | -                     | B                         |
| <b>Small Pore</b>        |                       |                           |
| 17                       | Ga, Ge                | -                         |
| 18                       | As, Ga, Ge, Ti        | -                         |
| 34                       | Be, Li                | As, B, Be, Ga, Ge, Li, Ti |
| 35                       | -                     | As, B, Ge, Ti             |
| <b>Very Small Pore</b>   |                       |                           |
| 20                       | Be, Ga, Ge, Li, Ti    | Be, Ga                    |

aluminophosphates, 17 and 20. The SAPO anhydrous composition is  $0-0.3R \cdot (Si_xAl_yP_z)O_2$ , where the mole fraction of silicon, x, typically varies from 0.04 to 0.20 depending on synthesis conditions and structure type. Their adsorption properties, pore sizes, and thermal and hydrothermal stability resemble those of the AlPO<sub>4</sub> molecular sieves. The SAPO's exhibit a range of moderate to high hydrophilic surface selectivity encompassing those shown by the AlPO<sub>4</sub>'s and zeolites. Their catalytic properties are mildly to strongly acidic depending on silicon concentration and structure type.

If one considers the SAPO compositions in terms of silicon substitution into a hypothetical aluminophosphate framework, the predominant substitution mechanism appears to be silicon substitution for phosphorus (1), with some substitution of two silicons

for an aluminum plus phosphorus (2). Mechanism (1) leads to SAPO compositions having anionic frameworks with a net negative charge with concomitant cation exchange properties and potential for Bronsted acid sites. Table 5 shows typical compositions for SAPO-5, SAPO-11, SAPO-34 and SAPO-37. SAPO-34 and -37 with mole fractions  $y = 0.5$  and  $(x+z) = 0.5$  illustrate an ideal mechanism (1). SAPO-5 and -11 with  $(x+z)$  greater than 0.5 illustrate the combined (1) and (2) mechanisms.

TABLE 5. Typical SAPO and MeAPO Framework Composition,  $\text{TO}_2^a$

| SAPO Species | $(\text{Si}_x \text{Al}_y \text{P}_z)\text{O}_2$ | Net Framework Charge/ $\text{TO}_2$ | MeAPO Species | $(\text{Me}_x \text{Al}_y \text{P}_z)\text{O}_2$ | Net Framework Charge/ $\text{TO}_2$ |
|--------------|--|-------------------------------------|---------------|--|-------------------------------------|
|              | x y z  |                                     |               | x y z  |                                     |
| 5            | 0.14 0.45 0.41                                   | -0.04                               | 5             | 0.08 0.42 0.50                                   | -0.08                               |
| 11           | 0.14 0.44 0.42                                   | -0.02                               | 36            | 0.09 0.42 0.49                                   | -0.11                               |
| 34           | 0.13 0.50 0.37                                   | -0.13                               | 11            | 0.08 0.42 0.50                                   | -0.08                               |
| 37           | 0.16 0.50 0.34                                   | -0.16                               | 44            | 0.14 0.36 0.50                                   | -0.14                               |
|              |  |                                     | 20            | 0.16 0.33 0.51                                   | -0.14                               |

<sup>a</sup>From elemental analysis, for divalent Me. Net framework charge calculated from  $\text{TO}_2$  formula.

**Metal aluminophosphates (MeAPO).** In the metal aluminophosphate (MeAPO) family, the framework composition contains metal, aluminum and phosphorus. The metal (Me) species include the divalent forms of Co, Fe, Mg, Mn and Zn, and trivalent Fe. As in the case of SAPO, the MeAPO's exhibit both structural diversity and an even more extensive compositional variation. The thirteen structure-types crystallized in the MeAPO family include framework topologies related to the zeolites, e.g., 34 and 35, and to the  $\text{AlPO}_4$ 's, e.g., 5 and 11, as well as novel structures, e.g., 36 (0.8nm pore) and 39 (0.4nm pore). In general, any of the five metals can be used to synthesize any of the observed structures. The MeAPO's represent the first demonstrated incorporation of divalent elements into microporous frameworks.

The spectrum of adsorption pore sizes and pore volumes and the hydrophilic surface selectivity of the MeAPO's are similar to those described for the SAPO's. The observed catalytic properties vary from weakly to strongly acidic, and are both metal and structure dependent. The thermal and hydrothermal stability of the MeAPO materials is somewhat less than that of the  $\text{AlPO}_4$  and SAPO molecular sieves.

The MeAPO molecular sieves exhibit a wide range of compositions within the general formula,  $0-0.3\text{R}(\text{Me}_x\text{Al}_y\text{P}_z)\text{O}_2$ . The value of x, the mole fraction of Me, typically varies from 0.01 to 0.25. The organic template, R, again is an amine or quaternary ammonium species occupying the structural voids. Using the same mechanistic concepts described for SAPO, the MeAPO's can be considered as hypothetical  $\text{AlPO}_4$  frameworks that have undergone substitution. In contrast to the mechanism observed for the SAPO's, in the MeAPO's the metal appears to substitute exclusively for Al rather than P. This mode of substitution, divalent or trivalent metal for trivalent aluminum, results in a net negative ( $\text{Me}^{2+}$ ) or neutral ( $\text{Me}^{3+}$ ) framework charge. Like SAPO, the negatively charged MeAPO frameworks possess ion exchange properties and the potential for Bronsted acid sites.

Representative compositions for MeAPO-5, -36, -11, -44, and -20 are shown in Table 5 in support of this substitutional mechanism. The framework stoichiometry in all cases shows that z, the mole fraction of P, is 0.5, and therefore the sum of x and y, the mole fraction of Me and Al, respectively, is 0.5.

**Other framework compositions.** The MeAPSO family (ref. 18) further extends the structural diversity and compositional variation found in the SAPO and MeAPO molecular sieves. These quaternary frameworks have Me, Al, P, and Si as framework species. The MeAPSO structure types include framework topologies observed in the binary ( $\text{AlPO}_4$ ) and ternary (SAPO and MeAPO) compositional systems, and the novel structure 46 (0.7nm pore, structure determined, ref. 15).

In the ELAPO (ref. 19, 20) and ELAPSO (ref. 18, 21) compositions the additional elements, Li, Be, B, Ga, Ge, As, and Ti are incorporated into the framework structures. Table 4 includes examples of structures with large, intermediate, and small pore sizes for most of the added elements.

Quinary and senary framework compositions have been synthesized containing aluminum, phosphorus and silicon, with additional combinations of divalent (Me) metals (ref. 22). Other workers recently reported the synthesis of  $\text{AlPO}_4$ -based molecular sieves described as containing several additional framework elements (ref. 23).

### Synthesis

The aluminophosphate-based molecular sieves are synthesized by hydrothermal crystallization of reactive aluminophosphate gels containing the additional framework elements and an organic template, at temperatures from 373 to 523K. The optimum crystallization temperature depends on composition and structure. The  $AlPO_4$  and SAPO materials tend not to crystallize at temperatures below 398K, whereas several of the MeAPO species crystallize readily at 373K.

The organic template appears to play a critical structure-directing role. The template is trapped or clathrated in the structural voids as the crystals grow. Over eighty-five amines and quaternary ammonium species have been used successfully as crystallization templates, including primary, secondary, tertiary and cyclic amines, and alkanolamines. The degree of template-structure specificity varies from the crystallization of  $AlPO_4-5$  with twenty-three templates to the formation of  $AlPO_4-20$  with only one template (ref. 17). Table 6, a summary of typical templates forming the major structures, amply illustrates one template forming many structures (11, 31, 41 and 46 with di-n-propylamine). Here, structure control is exercised by other synthesis variables such as temperature, template concentration, gel oxide composition, and pH. The influence of the template is both steric and electronic, and typically exhibits the neat stoichiometry and space-filling characteristics illustrated for  $AlPO_4-5$  and 11.

The initial gel pH in most cases is weakly acidic facilitating the successful incorporation of the hydrolyzable metal cation form of the elements into the frameworks, and inhibiting their precipitation as spurious hydroxides or oxides.

TABLE 6. Structure-Template Relationships

| Structure Type           | Typical Template(s)                       | Structure Type         | Typical Template(s)      |
|--------------------------|---|------------------------|--------------------------|
| <b>Large Pore</b>        |   | <b>Small Pore</b>      |                          |
| 5                        | tetrapropylammonium, tri-n-propylamine    | 14                     | isopropylamine           |
| 36                       | tri-n-propylamine                         | 17                     | quinuclidine, piperidine |
| 37                       | tetrapropylammonium + tetramethylammonium | 18                     | tetraethylammonium       |
| 46                       | di-n-propylamine                          | 34                     | tetraethylammonium       |
|                          |   | 35                     | quinuclidine             |
|                          |   | 44                     | cyclohexylamine          |
|                          |   | 47                     | diethylethanolamine      |
| <b>Intermediate Pore</b> |   | <b>Very Small Pore</b> |                          |
| 11                       | di-n-propylamine, di-iso-propylamine      | 20                     | tetramethylammonium      |
| 31                       | di-n-propylamine                          |                        |                          |
| 41                       | di-n-propylamine                          |                        |                          |

### Catalytic properties

The catalytic properties of the new molecular sieve materials were assessed with n-butane cracking as a probe for Bronsted acidity (ref. 24). The pseudo first order rate constants for a number of species of aluminophosphate-based materials are shown in Table 7.

TABLE 7. n-Butane Cracking Over  $AlPO_4$ -based Molecular Sieves<sup>a</sup>

| Species     | $k_A$     | Species  | $k_A$     | Species   | $k_A$     |
|-------------|-----------|----------|-----------|-----------|-----------|
| $AlPO_4-5$  | ~0.05     | MAPO-36  | 11 - 24   | ZAPO-34   | 13        |
| BeAPO-5     | 3.4       | CoAPO-36 | 11        | SAPO-34   | 0.1 - 7.6 |
| CoAPO-5     | 0.4       | MnAPO-36 | 6.8       | BeAPSO-34 | 7.6       |
| MAPO-5      | 0.5       | MAPSO-36 | 18        | GAPSO-34  | 10.0      |
| MnAPO-5     | 1.2       |          |           |           |           |
| SAPO-5      | 0.2 - 16  | BeAPO-34 | 3.7       | MAPO-39   | 0.05      |
| MAPSO-5     | 2.6       | CoAPO-34 | 5 - 15    |           |           |
| ZAPSO-5     | 1.5       | FAPO-34  | 0.1 - 0.6 |           |           |
| $AlPO_4-11$ | <0.05     | MAPO-34  | 7 - 29    | Chabazite | ~7        |
| SAPO-11     | 0.5 - 3.5 | MnAPO-34 | 2.5 - 5.2 | $NH_4Y$   | ~2        |

<sup>a</sup> $k_A$  is typical pseudo first order rate constant in ( $cm^3/min-gram$ ). See reference 24 for description of n-butane cracking test. Zeolites are for reference.

The materials exhibit activities that are both structure and metal dependent. The incorporation of metal in the 5 structure imparts low activity, whereas the incorporation of Si results in a range of low to moderately high activities. Incorporation of magnesium into the 36 and 34 structures leads to moderate to high activity. Among the MeAPO-34's each metal possesses its own unique range of activities. The low activity of MeAPO-39 is consistent with its small pore excluding n-butane from the intracrystalline voids, and establishes that the external surfaces of MeAPO's do not contribute to the activity.

Most of the compositions are free of alkali metals in contrast to the zeolites, and the catalytic activity and acid sites are generated simply by calcination of the materials to remove the organic template and H<sub>2</sub>O.

### Crystal chemistry

The richness of the crystal chemistry observed in the AlPO<sub>4</sub>-based molecular sieves is remarkable. Microporous frameworks containing elements with oxidation states of +1 (Li), +2 (Me, Be), +3 (B, Al, Fe, Ga), +4 (Si, Ge, Ti) and +5 (As, P), and containing as many as six framework elements have been crystallized. The framework siting of many of the elements is consistent with their known crystal chemistry and Pauling's radius ratio concepts (ref. 25). The surprising framework elements not normally predisposed to tetrahedral coordination with oxygen or falling outside of the tetrahedral radius ratio are exemplified by Li, Co, Mg, Mn and Zn. Their successful incorporation into the molecular sieve frameworks may be due to the flexibility of the microporous structure and specific interactions with the organic template, coupled with the mildly acidic gel chemistry used in their synthesis.

Tielen et al (ref. 26) recently reviewed the substitution of other framework elements into zeolites and silica molecular sieves and conclude that there is substantial evidence for the substitution of Ge<sup>4+</sup>, B<sup>3+</sup>, Ga<sup>3+</sup>, Be<sup>2+</sup>, and P<sup>5+</sup> into the frameworks of these molecular sieves. They conclude that the claimed substitution of other elements is not sufficiently substantiated and that based on radius ratio concepts, their tetrahedral siting is not predicted. The fewer number of framework elements in the zeolites and silica molecular sieves may be due to the basic pH prevalent in synthesis. The high pH favors the precipitation of many of the substitutional elements as extraneous oxides or hydroxides.

### Evidence of framework siting

Various characterization techniques provide supporting evidence for the framework siting of the elements. Adsorption properties establish the purity and lack of pore plugging, and coupled with x-ray powder diffraction the absence of impurity phases. Chemical analysis provides the framework stoichiometry which supports reasonable substitutional mechanisms as illustrated for SAPO and MeAPO compositions.

The Bronsted acidity is enhanced by the addition of other framework elements to the AlPO<sub>4</sub> composition. Extraneous oxides and hydroxides in general do not enhance Bronsted acidity. The crystallization of novel structures accompanying the addition of a framework element was shown for the SAPO, MeAPO and MeAPSO compositions and provides strong evidence of framework incorporation.

SEM/EDX has been an invaluable tool to establish the homogeneity and semi-quantitative analysis of individual particles. Particles can be identified with a specific structure type from their known morphology. The hydroxyl region infrared shows additional OH structure due to framework incorporation of the elements Me and Si. Solid state NMR has provided direct or indirect evidence of tetrahedral siting of Al, P, Mg, Si, Li, B, Zn and Ga. Optical and ESCA-AUGER spectroscopy indicate tetrahedral coordination for Co<sup>2+</sup>, Mn<sup>2+</sup> and Mg<sup>2+</sup>. In addition, the Co-containing compositions are a brilliant deep blue characteristic of Co<sup>2+</sup> in tetrahedral coordination.

The amount of evidence for framework incorporation varies among the elements and is largely a function of the extent of investigation, but in all cases appears to be sufficient.

## CONCLUSION

The AlPO<sub>4</sub>-based molecular sieves are a landmark discovery in new generations of molecular sieves. Their number and scope provides a plethora of new materials for research investigation by present and future generations of molecular sieve scientists. The remarkable diversity in crystal structure and crystal chemistry offers a nearly unlimited number of design parameters to tailor adsorptive and catalytic properties.

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