

The Structure of Zeolite and Aluminophosphate Molecular Sieves*

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Zeolites and other molecular sieves are microporous crystalline solids whose main uses are in catalysis, ion-exchange reactions and as adsorbents. Their crystalline structures and different ways of identification of molecular sieve structure are reviewed, together with a short introduction into the catalytic activity of these materials. Synthesis and structural overview of aluminophosphates, a new and fast-growing family of microporous materials, are presented and strategy for introducing different metal atoms into aluminophosphate framework is discussed. These chemical framework modifications lead to a broad range of structure types and offer a nearly unlimited number of design parameters for the tailoring of catalytic and adsorptive properties of aluminophosphate materials. Our results in the areas of synthesis and X-ray diffraction structural characterization of metal-substituted aluminophosphates are reviewed.

INTRODUCTION

Zeolites and other molecular sieves are a class of materials that are finding widespread application in diverse areas, such as catalysis, ion-exchange and separation processes and as drying agents. The close connection between the microscopic structure and the macroscopic properties of these materials allows one to use molecular sieves to recognize, discriminate and synthesize molecules with precision that can be less than 1 Å and, as a result, molecular sieves are drawing attention in all fields of molecular recognition phenomena.¹ The properties of these materials stem directly from the characteristics of their crystal structure and this is what makes zeolite crystallography an especially rich and rewarding field of research. There are extensive books on zeolites and molecular sieves.²⁻⁶ Additionally, mention should be made of an excellent review article on Zeolite Crystallography by Lynne B. McCusker⁷ and an introduction into the field of zeolites by John M. Newsam.⁸

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Since the initial discovery of the synthetic zeolite A, X and Y, major advances have occurred in the synthesis of molecular sieve materials and a great number of new methods have evolved for the identification and characterization of these materials. Besides an ever growing list of aluminosilicate zeolites, molecular sieves containing other elemental compositions have been prepared. These materials differ in their catalytic activity relative to the aluminosilicate zeolites and have the potential of tailoring the molecular sieve catalysts for specific applications. Elements such as B^{3+} , Ga^{3+} , Fe^{3+} and Cr^{3+} have been proposed as substitutes for Al^{3+} in the framework lattice during the synthesis, while Ge^{4+} and Ti^{4+} usually replace Si^{4+} .

A new class of microporous, crystalline materials are the aluminophosphate ($AlPO_4-n$)⁹ molecular sieves. Discovered in 1982, structural analogues of zeolites as well as new structural types have been prepared, including the species with a pore size greater than those known in aluminosilicate zeolites. These materials have no ion exchange capacity due to their balanced framework charge. Initially, silicon was incorporated into the $AlPO_4$ structures¹⁰ and its incorporation as well as that of other ions, such as magnesium, zinc, cobalt and manganese, led to the discovery of new structures and gave new possibilities of controlling the catalytic and adsorptive properties of these materials. Addition of structural silicon and other heteroatoms introduces negative charge into the framework, thus enhancing hydrophilicity and catalytic acid activity, as well as resulting in ion exchange capacity.

ZEOLITES AND ZEOLITE-LIKE MATERIALS

In 1756, the Swedish mineralogist A. F. Cronsted heated an unidentified silicate mineral and observed that it fused readily in a blowpipe flame with marked intumescence. He called the minerals that behaved in this manner zeolites¹¹ derived from the Greek words »zeo« (to boil) and »lithos« (stone). Since then, approximately 40 natural zeolites have been discovered. Classically, zeolites are defined »as class of crystalline aluminosilicates with (i) relatively rigid anionic aluminosilicate framework with well-defined channels and cavities; (ii) mobile interchangeable cations (usually group 1 or 2) which balance the negative charge of the framework; and (iii) water which can be removed by heating or evacuating without affecting the framework topology« (Ref. 7). This definition has recently been somewhat relaxed to encompass a broader class of related microporous materials. Thus, any three-dimensional framework structure with tetrahedrally co-ordinated atoms (T atoms) joined to each other through oxygen bridging atoms and with a framework density of less than 21 T atoms/1000 Å³ can be considered zeolite-like.¹²

With the recent discoveries of molecular sieve materials containing other elements in addition to, or instead of, aluminium and silicon, the casual interchange of the term »molecular sieve« and »zeolite« must be reconsidered. In 1932, McBain proposed the term »molecular sieve« to describe a class of materials that exhibited selective adsorption properties.¹³ For a material to be a molecular sieve, it must separate components of a mixture on basis of molecular size and shape differences. In 1932, only two classes of compounds exhibiting these properties were known: zeolites and certain microporous charcoals. Nowadays, many new materials are known whose regular framework structures will separate components of a mixture on the basis of size and shape, such as silicates, metasilicates, metalloaluminates, aluminophosphates (AlPOs), silicoaluminophosphates (SAPOs), metalloaluminophosphates (MeAPOs), ELAPOs, ELAPSOs, MeAPSOs,... The difference between these ma-

terials is their elemental composition and very often not their structure since many are structurally analogous.

THE STRUCTURE OF ZEOLITES

Zeolites are hydrated, crystalline tectoaluminosilicates that are built of TO_4 tetrahedra (T = tetrahedral species, Si, Al, P, *etc.*) and each apical oxygen atom is shared with an adjacent tetrahedron, thus giving a framework ratio of O/T = 2. Various structures of SiO_2 do not contain framework charge since silicon is tetravalent. Zeolite aluminosilicates, on the other hand, possess negatively charged oxide frameworks (one charge per framework Al^{3+}) and more open structures with water or larger molecules in the channels and cavities of the structure and with extraframework counter-balancing positive ions, which can readily be exchanged. Typical cations in natural zeolites are alkali and alkaline earth ions. Synthetic zeolites may contain also organic cations, such as quaternary ammonium ions. Presently, there are approximately 85 molecular sieve structures known¹⁴. The Structure Commission of the International Zeolite Association assigns a three-letter code to each new framework topology.

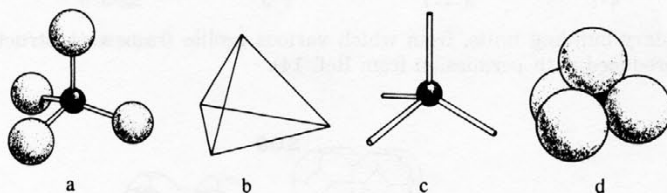


Figure 1. A TO_4 tetrahedron, the primary building unit of all zeolite structures (reproduced with permission from Ref. 2).

Individual TO_4 tetrahedra (Figure 1) in zeolite structures are usually close to regular, but the shared oxygen linkage can accommodate a wide range of T–O–T bond angles from approx. 125° to 180° . The tetrahedra are combined together to form a variety of structures. TO_4 tetrahedra are primary building units in all zeolite structures, but when various full structure types are examined, similarities and relationships between them become apparent. The majority of the observed frameworks can be constructed from one type of the so called secondary building units (SBU; Figure 2) which means that these secondary building units, which contain up to 16 T atoms, are derived assuming that the entire framework is made up of one type of SBU only and a unit cell always contains an integral number of SBUs. Actually, many structures can be described by more than one type of SBU and sometimes two types of SBUs are needed to make up the framework.

Zeolite framework structures can also be constructed from different polyhedra. Figure 3 illustrates how different zeolite structures can be obtained from the truncated cuboctahedron, which also represents the sodalite or β -cage. This and other different observed types of cages lead to a consideration of other possible ways in which they could be interconnected, leading also to new hypothetical framework structures.

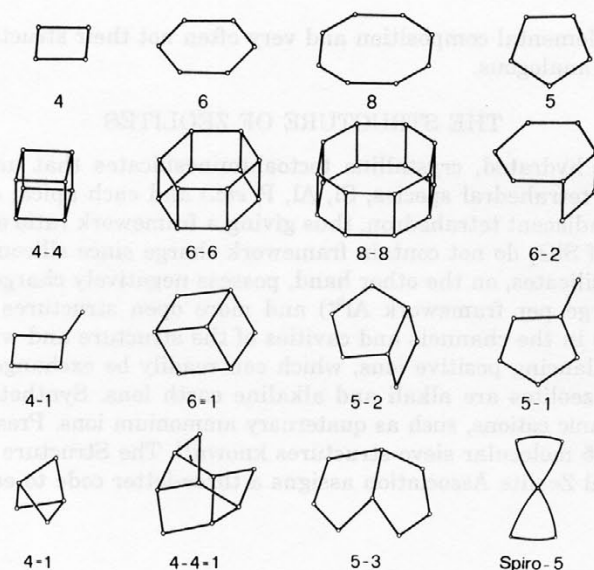


Figure 2. Secondary building units, from which various zeolite framework structures can be constructed (reproduced with permission from Ref. 14).

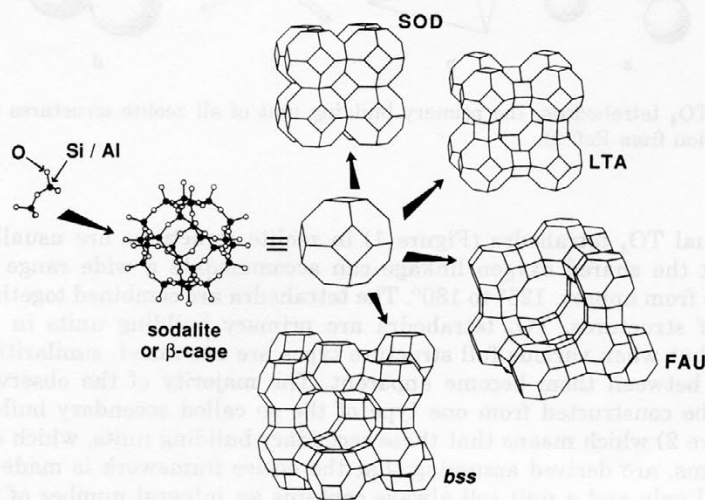


Figure 3. Construction of four different zeolite frameworks containing a sodalite or β -cage (reproduced with permission from Ref. 8).

Another possibility of discussing the zeolite framework structures is based on the fact that many zeolite structures, when viewed in projection along one or more crystallographic directions, appear as 2-dimensional 3-connected nets (Figure 4). Dif-

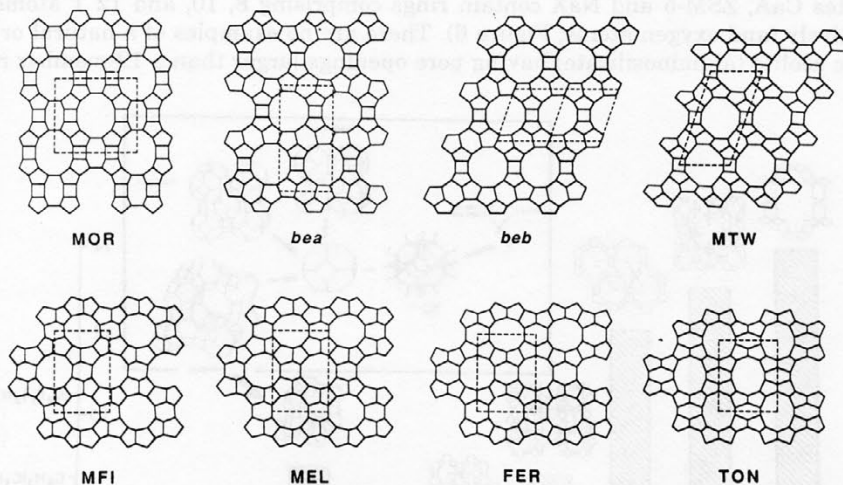


Figure 4. Eight zeolite structures projected along principal crystallographic directions. The dashed lines indicate the unit cell outlines (reproduced with permission from Ref. 8).

ferent modes of inter-sheet connections are generally possible and the families of 2-D 3-connected nets thus provide a basis for generating hypothetical zeolite structures. The character of the stacking of sheets along one axis is a good means of classifying many of the known zeolite structures types (examples in Ref. 8).

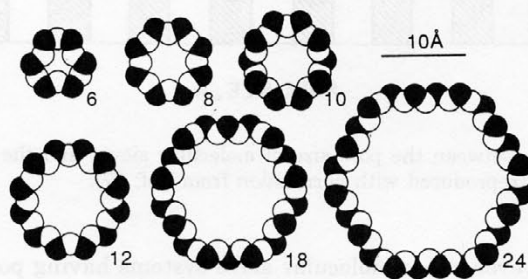


Figure 5. Aperture dimensions (pore size) depend primarily on the number of T or O atoms in the ring (reproduced with permission from Ref. 8).

Channel opening or pore size is often described in terms of an n -ring (Figure 5). A 6-ring for example is a ring containing 6 T atoms and 6 O atoms, though this ring would usually be classified as having 6 T atoms (not mentioning O atoms). In aluminosilicate zeolites, there are only three groups of pore openings that are of practical interest for catalytic applications and they are also referred to as small (8-member ring), medium (10-member ring) and large (12-member ring). As an example,

zeolites CaA, ZSM-5 and NaX contain rings comprising 8, 10, and 12 T atoms, respectively (and oxygen atoms; Figure 6). There are no examples of a natural or synthetic zeolite (aluminosilicate) having pore openings larger than a 12-member rings.

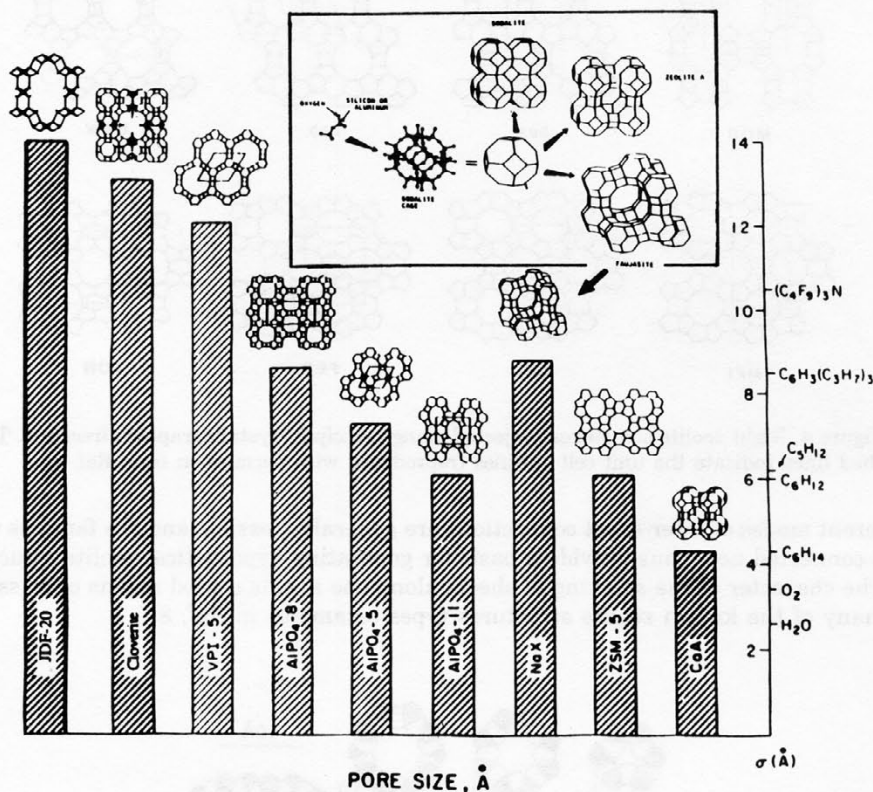


Figure 6. Correlation between the pore size of molecular sieves and the kinetic diameter (σ) of various molecules (reproduced with permission from Ref. 67).

There are, however, other molecular sieve systems having pore openings larger than those observed so far in zeolites. In 1988, Davis *et al.* reported an aluminophosphate material called VPI-5^{15,16} that contained an 18-member ring with pore size of approximately 13 Å. With this material, the range of pore size of crystalline molecular sieves expanded significantly. Davis *et al.*¹⁷ also proposed for the molecular sieves containing ring sizes above 12 to be called extra-large pore materials. After VPI-5, three other extra-large pore materials have appeared: AIPO₄-8, cloverite and JDF-20.

Shortly after the discovery of VPI-5, it was shown that some samples of VPI-5 could be partly or wholly converted to AIPO₄-8.^{18,19} Independent structure determinations by two groups^{20,21} revealed 14-member rings in the AIPO₄-8 material. This material forms via phase transition from VPI-5 and shows very little microporosity because of faults in the structure that block one-dimensional pores.

Cloverite, a gallophosphate, is another extra-large pore molecular sieve that contains rings consisting of 20 tetrahedrally-co-ordinated atoms²² in the shape of a four-leaved clover (Figure 7) and a three-dimensional channel system. The unusual shape of window is due to the presence of terminal hydroxyl groups in the framework and provides new possibilities for shape-selective sorption. The supercage formed at the

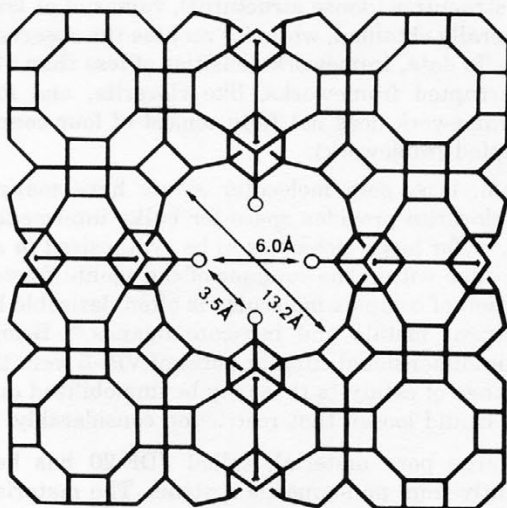


Figure 7. A projection of the pseudo unit cell of cloverite along the [100] direction, showing the cloverleaf-shaped 20-atom pore opening (reproduced with permission from Ref. 22).

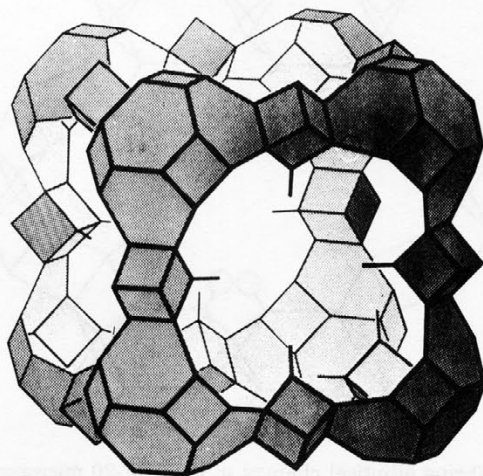


Figure 8. A skeletal drawing of the large supercage of the framework structure in cloverite (reproduced with permission from Ref. 22).

intersection of the channels has a body diagonal of 29–30 Å (Figure 8) and can thus accommodate larger intermediates in zeolite catalytic processes. This new gallophosphate molecular sieve has an extremely open structure with its framework density of only 11.1 tetrahedral atoms per 1000 Å³, as compared with 12.7 for faujasite, which has the lowest framework density known so far. Brunner and Meier²³ have listed all known zeolite structures and compared their framework densities. For non-zeolitic framework structures (dense structures), values of at least 20 to 21 T atoms per 1000 Å³ are generally obtained, while for zeolites the observed values range from 12.7 to around 20.5. To date, framework densities of less than 12 have been encountered only for interrupted frameworks, like cloverite, and for hypothetical networks.²⁴ (When a framework does not fully consist of four connected tetrahedra, it is called an interrupted framework).

Multidimensional, large-pore molecular sieves have many advantages.²⁵ The large supercage in cloverite provides space for bulky intermediates to form during a catalytic reaction, or for large molecules to be synthesized *in situ*. Such molecules can act as catalytic sites within the confines of the zeolite framework and the trapping, or immobilization of complex molecules is often desirable because of the interest in their constituent metals and intricate ligands.²⁶ Before the discovery of cloverite, the 13 Å unidimensional circular pores of VPI-5 were the largest available, which limited the range of catalysts that may be immobilized and the cloverite's expanded, 30 Å cage, should loosen that restriction considerably.

Another extra-large pore material, called JDF-20 has been synthesized recently,²⁷ predominantly from non-aqueous systems. The material has aluminophosphate composition and an elliptically-shaped main 20-member ring channel (Figure 9), with oxygen atoms projecting into the channel.

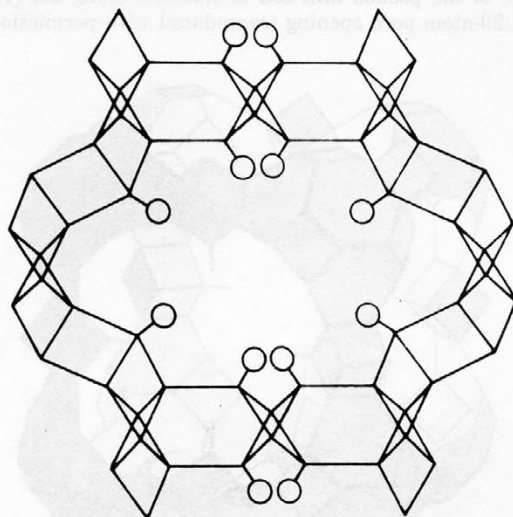


Figure 9. View of the 20-ring elliptical channel in the JDF-20 microporous aluminophosphate material (reproduced with permission from Ref. 27).

Microporous framework solids, discussed so far, can adopt pore dimensions up to approx. 14 Å. Mesoporous inorganic solids (with pore diameters in the 20–500 Å range) have also found great utility as catalysts and sorption media, and the examples include silicas and modified layered materials. These materials are invariably amorphous or paracrystalline, with pores that are irregularly spaced and broadly distributed in size. Recently, a research group from the Mobil Research and Development Corporation²⁸ reported on the synthesis of mesoporous solids from the calcination of aluminosilicate gels in the presence of surfactants (Figure 10). The resulting materials possess regular array of uniform channels, the dimensions of which can be tailored (in the range from 16 to 100 Å or even more) through the choice of surfactant, other chemicals and reaction conditions. Figure 10 shows MCM-41, a member of this family of materials, with cylinder-to-cylinder repeat distances about 40 Å.²⁸

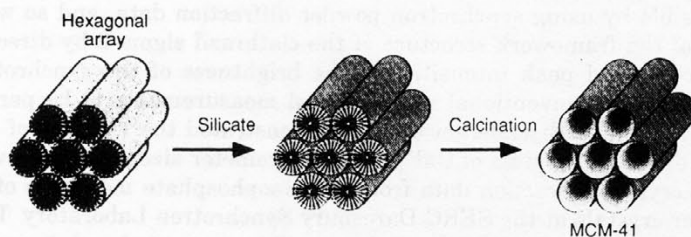


Figure 10. Schematic drawing of the liquid-crystal templating mechanism. Hexagonal arrays of the cylindrical micelles form, with the polar side of the surfactants to the outside. Silicate species then occupy the spaces between the cylinders. The final calcination burns off the original organic material, leaving hollow cylinders of inorganic material (reproduced with permission from Ref. 28).

IDENTIFICATION OF THE MOLECULAR SIEVE STRUCTURE

Two techniques are essential for identification of a molecular sieve structure: the X-ray powder diffraction and adsorption capacity measurements. Ideal diffraction patterns have been calculated for most of the known zeolite structures and, together with other crystal data, these diffraction patterns are collected in the publication of the Structure Commission of the International Zeolite Association, compiled by von Ballmoos and Higgins.²⁹ X-ray powder diffraction indicates the uniqueness of the structure, as the powder diffraction pattern is a fingerprint of the individual structure. This method also provides information on the presence of either a single phase or a mixture of phases in the sample (phase purity), which can be used for quality control in preparation of a particular type of known zeolite material. The powder pattern can also provide information on the degree of crystallinity. Unit cell volume can be calculated from powder patterns and, being sensitive to the amount of aluminium atoms in the tetrahedral structural sites, can give information about the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the aluminosilicate zeolite material. It can also supply information about the incorporation, as well as the degree of incorporation, of other elements into structural framework sites.

Determination of the crystal structure of an unknown zeolite material is usually difficult. Conventional single crystal X-ray or neutron diffraction is often possible for natural mineral samples³⁰ or for aluminophosphate samples, which sometimes crystallize as larger crystals (over 0.1 mm). Synthetic zeolites are almost invariably microcrystalline, and problems of phase purity, inhomogeneity and defects or disorder of various types are common. Therefore, the X-ray powder diffraction is used frequently in zeolite structure solution and refinement.³¹ Refinement can be based on integral peak intensities, but more often the Rietveld³² analysis of full diffraction profile is used.

Very bright synchrotron X-ray sources offer significant advantages in diffraction studies of zeolites.³³ Powder diffraction patterns can be recorded faster and with much higher instrumental resolution, thus allowing more complicated structures to be refined by using Rietveld methods. Refinement of the structure of zeolite ZSM-11³⁴ was possible by using synchrotron powder diffraction data, and so was the determination of the framework structure of the clathrasil sigma-2 by direct methods based on decomposed peak intensities.³⁵ The brightness of the synchrotron X-ray sources permits also conventional single-crystal measurements to be performed on much smaller crystals. Eisenberger *et al.*³⁶ demonstrated the viability of diffraction experiments on single crystals of CaF₂ of the micrometer size, and we have also collected single crystal diffraction data from aluminophosphate materials of the 20 to 30 micrometer crystals at the SERC Daresbury Synchrotron Laboratory. The results of our data collections and structure analyses will be presented and discussed in the part describing our work later on.

Adsorption capacity measurement is second characterization technique that provides a lot of information about the molecular sieve structure. The absorption capacity of oxygen, water or some other probe molecule supplies information on the amount of void volume within the sieve. It is also sensitive to the crystallinity of the samples. The less crystalline the sample, the less capacity it has. By selecting adsorbates with different kinetic diameters (σ) of the molecules (*cf.* Figure 6), information on the size of the molecular sieve pore openings can be quickly obtained. This information is more readily obtainable than the complete structure determination from X-ray diffraction and it is even more important if the actual crystal structure has not been determined. There is also some other information from the adsorption properties: water adsorption provides information on the hydrophobicity or hydrophilicity of the molecular sieve; the desorption of ammonia provides information on material acidity; diffusivity measurements indicate diffusion limitations and pore blockages.

There are other important methods that provide structural information about a newly synthesized molecular sieve. These characterization techniques are the infrared spectroscopy, extended X-ray absorption fine structure (EXAFS), magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR), electron paramagnetic resonance spectroscopy (EPR), UV-visible spectroscopy (especially for coloured metalloaluminophosphates), electron microscopy (SEM – scanning electron microscopy, STEM – scanning transmission electron microscopy, and HREM – high resolution electron microscopy), thermal methods, and chemical analysis (zeolite elemental composition is usually obtained by microprobe, by inductively coupled plasma emission spectroscopy (ICPES) or by atomic absorption spectroscopy).

THE USE OF ZEOLITES AND OTHER MOLECULAR SIEVES

The main areas in which zeolites and other molecular sieves are used are:

- catalysts and catalyst supports for numerous catalytically active metals,
- adsorbents and desiccants,
- molecular sieves in separation processes,
- ion-exchangers (especially in detergents),
- miscellaneous (waste water treatment, nuclear effluent treatment, animal feed supplements, soil improvement).

Catalytic zeolite applications have found greatest use in the hydrocarbon processing field in petroleum and petrochemical industry. The catalytic cracking is by far the largest application in the petroleum refining area (zeolite Y, ZSM-5), followed by hydrocracking (Y, Mordenite). Important applications are in hydro-isomerization and dewaxing (Mordenite, ZSM-5), while the well known Methanol-to-Gasoline (MTG) process for the production of synthetic fuel uses ZSM-5. Application of zeolites in the synthesis of organic fine chemicals is still underdeveloped (L. Moscow in Ref. 6). These potentials have been demonstrated for a variety of organic reactions, such as isomerization, aromatic substitution, oxidation and cyclization, showing the versatile character of zeolites in organic synthesis reactions.^{37,38} Nevertheless, a great progress has been made in the design of solid acid catalysts, which are considered to be important industrial materials.³⁹

CATALYTIC ACTIVITY OF ZEOLITES

The reactivity and the selectivity of zeolites as catalysts are determined by active sites provided by an imbalance in charge between the silicon and aluminium ions in the framework. Each aluminium atom in the zeolite framework induces a potential active acid site.⁴⁰ Brönsted and Lewis acid models of acidity have been used to classify the active sites in zeolites. In freshly synthesized material, the cations must be replaced by protons to produce the acid catalyst. Most of the recent high-silica zeolites are synthesized in the presence of large organic quaternary ammonium cations that remain within the channel system. After crystallization of the zeolite structure, they must be removed before ion exchange is possible. The organic cation is usually decomposed by a calcination process (thermal treatment for a few hours in air at temperatures between 500 and 600 °C). After this process, a mixture of alkali cations and some protons are still present. The remaining alkali cations are then removed by exchange treatment, either by hydrochloric acid (which may cause dealumination) or with an aqueous ammonium salt to produce the ammonium ion form. In Figure 11, a schematic diagram of the ion-exchange of zeolite mobile cations is shown, together with equilibrium between the Brönsted and Lewis acid sites.

Shape selectivity plays a very important role in molecular sieve catalysts.⁴¹ Regular channel structures with dimensions of pore openings comparable to the diameters of the molecules and high crystallinity are the principal advantages that molecular sieves offer over other catalytic materials. Shape selectivity operates by either reactant shape selectivity, product shape selectivity, or transition-state shape selectivity (Figure 12).

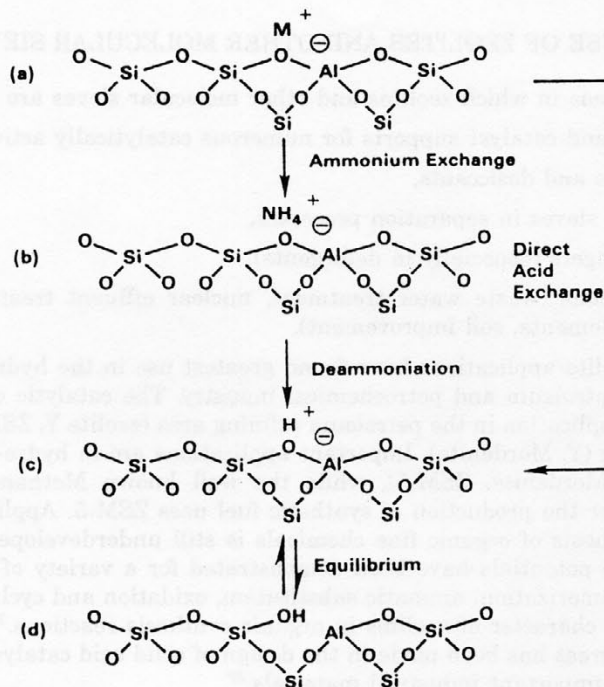


Figure 11. Diagram of the »surface« of a zeolite framework, with the as-synthesized form (a) and ammonium ion-exchanged form (b). Thermal treatment of the NH_4^+ form produces the H^+ or acid form (c, in equilibrium with d) (reproduced with permission from Ref. 5).

ALUMINOPHOSPHATES

Aluminophosphates were discovered in 1982 (the $AlPO_4$ family)⁹ and since then the compositional and structural diversity of $AlPO_4$ -based molecular sieves has continued to grow. To date, there are at least 27 different structures, and at least 14 elements, in addition to Al and P, have been incorporated into $AlPO_4$ -based frameworks.^{42,43} Some of the $AlPO_4$ structural types are zeolite analogues, while some are new structures.

The original choice of aluminophosphate chemistry for preparing a new family of molecular sieves was based in part on the extensive hydrothermal synthesis literature and the structural similarities of $AlPO_4$ to SiO_2 (S. T. Wilson in Ref. 6). Dense $AlPO_4$ phase exists in all structural polymorphs of SiO_2 – quartz, tridymite and cristobalite.

Comparison of $AlPO_4$ s and zeolites:

- $AlPO_4$ and Si_2O_4 have the same number of electrons,
- Al and P atoms are mainly tetrahedrally co-ordinated with O atoms,
- average ionic radius of Al^{3+} and P^{5+} is close to the ionic radius of Si^{4+} .

$AlPO_4$ molecular sieves contain Al and P in lattice T sites. Subsequently, other elements were incorporated and appropriate acronyms were introduced (SAPO – Si, Al,

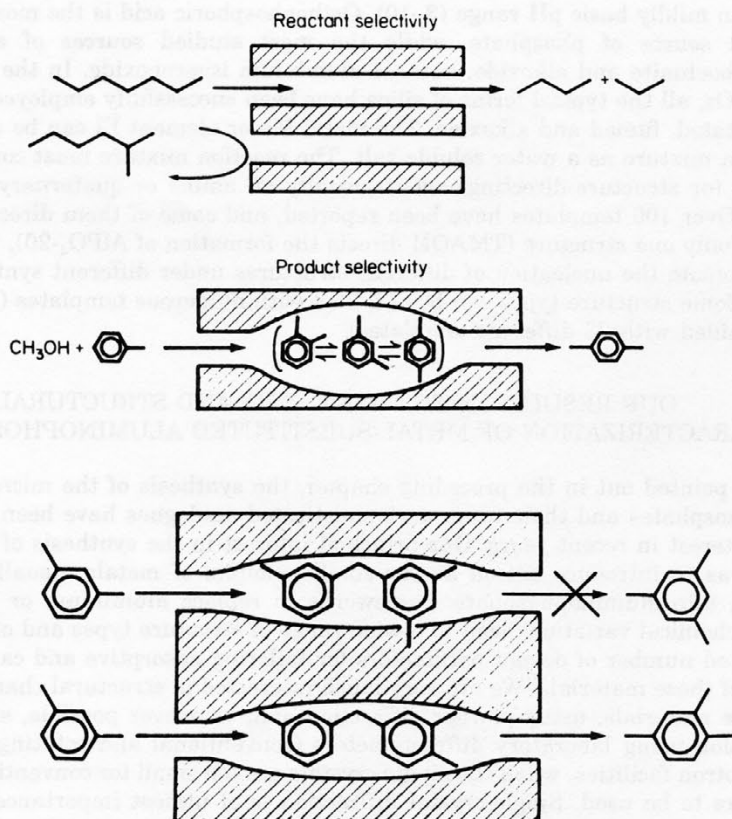


Figure 12. Diagram showing the three types of selectivity in zeolite-type catalysts: reactant, product and transition-state shape selectivity (reproduced with permission from Ref. 41).

P; MeAPO – Me (Co, Cr, Fe, Mg, Mn, Zn), Al, P; MeAPSO – Me, Al, P, Si; ElAPO – El (As, B, Be, Ga, Ge, Li, Ti), Al, P; ElAPSO – El, Al, P, Si). Chemical analysis, as well as structural and spectroscopic evidence elucidated the substitution patterns of many of these elements. All the structures are best described using a basic AlPO_4 framework with alternating Al and P sites. In SAPOs, the element Si replaces part of the P sites alone, or both Al and P sites. Divalent and trivalent elements substitute almost invariably into Al framework sites.

A wide variety of structure types have been observed within each compositional family and most have been determined. Each structure type has been designated with a number, and the same number is used regardless of the framework composition (e.g. AlPO_4 -5 and SAPO-5 have the same structure type). Of 27 structure-types so far identified, the largest class is small pore (14 structures with 8-member rings and two structures with 6-member rings), 3 structures with medium 10-member rings, 7 structures with large 12-member rings and 1 structure with a very large 18-member ring (VPI-5). Synthesis of aluminophosphates is usually in a mildly

acidic to mildly basic pH range (3–10). Orthophosphoric acid is the most frequently studied source of phosphate, while the most studied sources of alumina are pseudoboehmite and alkoxide, such as aluminium isopropoxide. In the preparation of SAPOs, all the typical forms of silica have been successfully employed – colloidal, precipitated, fumed and alkoxide. The metal Me or element El can be added to the reaction mixture as a water soluble salt. The reaction mixture must contain a templating (or structure-directing) agent, usually an amine or quaternary ammonium salt.⁴⁴ Over 100 templates have been reported, and some of them direct the formation of only one structure (TMAOH directs the formation of $\text{AlPO}_4\text{-20}$), while others will promote the nucleation of different structures under different synthesis conditions. Some structure types can be obtained with numerous templates ($\text{AlPO}_4\text{-5}$ can be obtained with 23 different templates).

OUR RESULTS IN THE SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF METAL-SUBSTITUTED ALUMINOPHOSPHATES

As pointed out in the preceding chapter, the synthesis of the microporous aluminophosphates and their framework-substituted analogues have been of considerable interest in recent years. Our principal interest in the synthesis of these materials was to introduce silicon and/or small amounts of metals, usually transition metals, into aluminophosphate frameworks to replace aluminium or phosphorus. These chemical variations lead to a wide range of structure types and offer a nearly unlimited number of design parameters for tailoring adsorptive and catalytic properties of these materials. We are very much interested in structural characterization of these materials, using powder diffraction and, whenever possible, single-crystal diffraction using laboratory diffractometers (conventional and rotating-anode) and synchrotron facilities, when the single crystals are too small for conventional diffractometers to be used. Single-crystal diffraction is of utmost importance for tracing small amounts of metals (in the order of 5 to 10%) that have replaced aluminium or phosphorus in the framework.

Preliminary characterization of a new aluminophosphate should include chemical analysis and powder diffraction and will sometimes allow the material to be assigned to an already known structure type, thus defining the connectivity of the framework atoms. Full structural characterization can be carried out in the three stages: (1) a detailed description of framework geometry, (2) definition of template molecule positions, and (3) identification of the sites where metal atoms have replaced a small proportion of aluminium or phosphorus atoms. To answer these questions from diffraction experiments is progressively more difficult for stages (1) to (3).

Very high resolution powder diffraction with synchrotron radiation has recently had great success with a number of zeolite and AlPO_4 materials^{45,46} but it is unlikely to get far beyond stage (1) when moderately complicated structures are involved. Single-crystal methods are therefore essential, but zeolite and AlPO_4 materials are well-known to yield only rather small single crystals; also common in these materials are small deviations of the framework geometry from higher symmetry arrangements, twinning or disorder, and disorder of template-molecule positions. As mentioned above, it should also be noted that the establishment of substitution of a first-row transition-metal for, say, 10% of the Al atoms at one site is equivalent to searching for one electron.

We have synthesized a number of sodalite-type AlPO_4 , SAPO, MeAPO and MeSAPO materials (Me = Co^{2+} and/or Zn^{2+}).^{47,48} While the Me^{2+} ions are in all cases constituents of the framework, most zinc-containing materials have a fraction of the Zn^{2+} ions located in the cavities. Powder diffraction analysis show that replacement of aluminium by silicon, cobalt and zinc, and phosphorus by silicon leads to an expansion of the parent aluminophosphate unit cell. Modification of AlPO_4 -20 and SAPO-20 with manganese²⁰ was inconclusive, as the EPR and DRS (diffuse reflectance spectroscopy) data for as-synthesized AlPO_4 -20(Mn) and SAPO-20(Mn) materials show the presence of octahedrally co-ordinated non-framework manganese.

In our attempts to prepare APOs and substituted APOs of new structural types, we used some amines that had not been previously reported to function as templates. One of such amines was hexamethylenetetraamine (HMTA).⁴⁹ Under the synthesis conditions, HMTA decomposes and the decomposition products influence the formation of AlPO_4 -15 and, in the presence of Co^{2+} , that of CoAPO -15. The Co^{2+} ion in CoAPO -15 occupies tetragonally deformed octahedral sites and this causes a slight expansion of the unit cell of CoAPO -15 in comparison to that of AlPO_4 -15, the structure of which was previously determined^{50,51} and shown to be an analogue of the mineral leucophosphate.⁵² The Co^{2+} ion was co-ordinated not only by the O atoms of the system but also by NH_3 molecules.

We have studied extensively the synthesis of the chabazite AlPO_4 -34 and SAPO-34 structure types. In the reaction system, in the presence of isopropylamine as a template, CoSAPO -14, as a new MeSAPO material, predominantly forms at 125 °C, while at 160 °C CoSAPO -34 is the main product.⁵³ CoSAPO -34 crystallized out from the system as single crystals of approximate dimensions of 10^{-3} mm³ and, therefore,

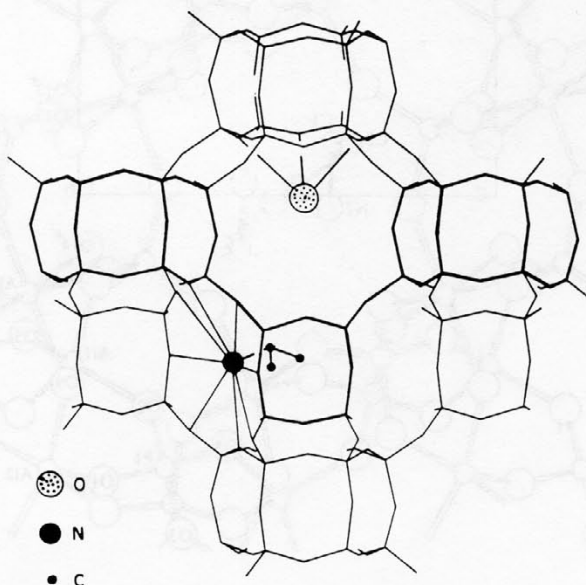


Figure 13. Diagram of the chabazite-like cage of CoSAPO -34. The two sites, occupied by water and isopropylamine molecules, are shown (reproduced with permission from Ref. 54).

it was possible to collect single-crystal data on a laboratory diffractometer and to determine the structure.⁵⁴ The framework structure is close to that of natural chabazite but with ordered tetrahedral sites, apparently (Al, Co) and (P, Si). The experimental evidence strongly supports the view that cobalt ions are incorporated in the framework. Each large cavity is occupied by one water molecule and by an isopropylamine molecule (Figure 13).

We have also tried to incorporate Mn^{2+} and Cr^{3+} into SAPO-34 framework.⁵⁵ Mn^{2+} ions incorporate into framework to give MnSAPO-34, while Cr^{3+} ions do not incorporate into the silicoaluminophosphate lattice. Calcination of MnSAPO-34 results in oxidation of Mn^{2+} and the calcination product can be reduced back to MnSAPO-34. The MnSAPO-34 material catalyzes the dehydration of methanol, and its catalytic activity is higher than that of SAPO-34.⁵⁵

We have studied the same reaction of methanol dehydration on SAPO-44 and MeSAPO-44 (Me = Co, Mn, Cr, Zn, Mg) materials.⁵⁶ Chabazite-type structures of MeSAPO-44 were extensively studied and prepared in diverse synthesis systems.^{57,58} It is interesting to note that in the reaction system with cyclohexylamine as a tem-

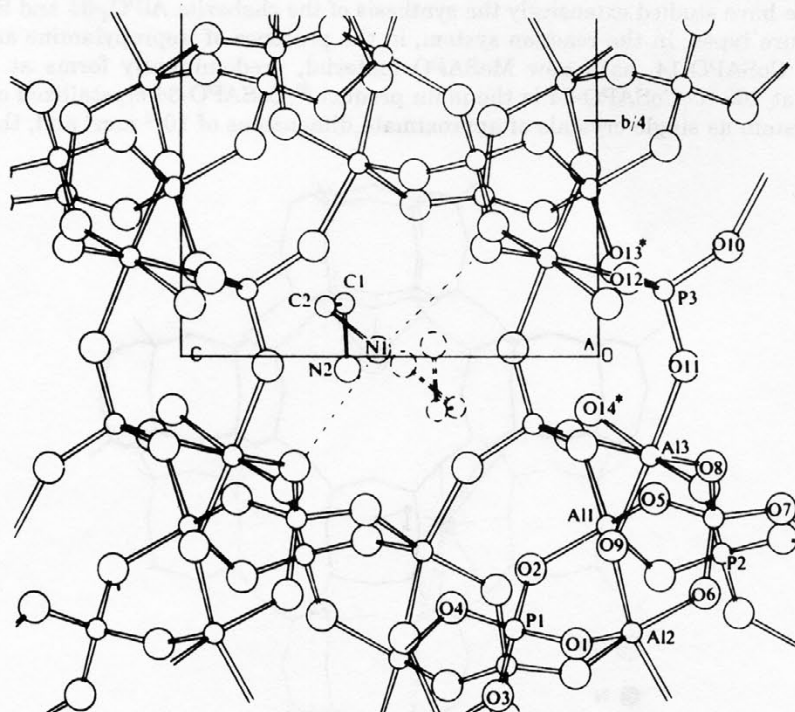


Figure 14. Projection of the part of the framework structure of CoAPO-21 along the a axis. Tetrahedral Al(1) site is partly occupied by Co atoms (reproduced with permission from Ref. 59).

plate, an intermediate solid layer-type crystalline phase was observed. In the case of CoSAPO-44 preparation, this »Co(APSO)_N« intermediate phase is indicated by electron spectroscopy to contain Co²⁺ in pentacoordinated environment. When (CoAPSO)_N is heated at 195 °C in a water suspension under autogeneous pressure, two processes occur: (a) a partial conversion of Co(APSO)_N into CoAPSO-44 and (b) decomposition of Co(APSO)_N into Co- and Al-phosphates. Thermal removal of cyclohexylamine at 270 °C from CoAPSO)_N and from (APO)_N, (APSO)_N and Mn(APSO)_N results in a breakdown of the respective crystal lattices.

We determined the crystal structure of CoAPO-21,⁵⁹ a cobalt-doped aluminophosphate related to AlPO₄-21, from a set of data collected by using synchrotron radiation. The crystals, obtained from the reaction mixture with ethylenediamine as a template, were relatively large for aluminophosphates and a crystal of 0.15 × 0.04 × 0.03 mm³ was used for data collection. The framework structure is similar to that of AlPO₄-21^{60,61} with 4-, 5- and 6-co-ordinate aluminium atoms. Substi-

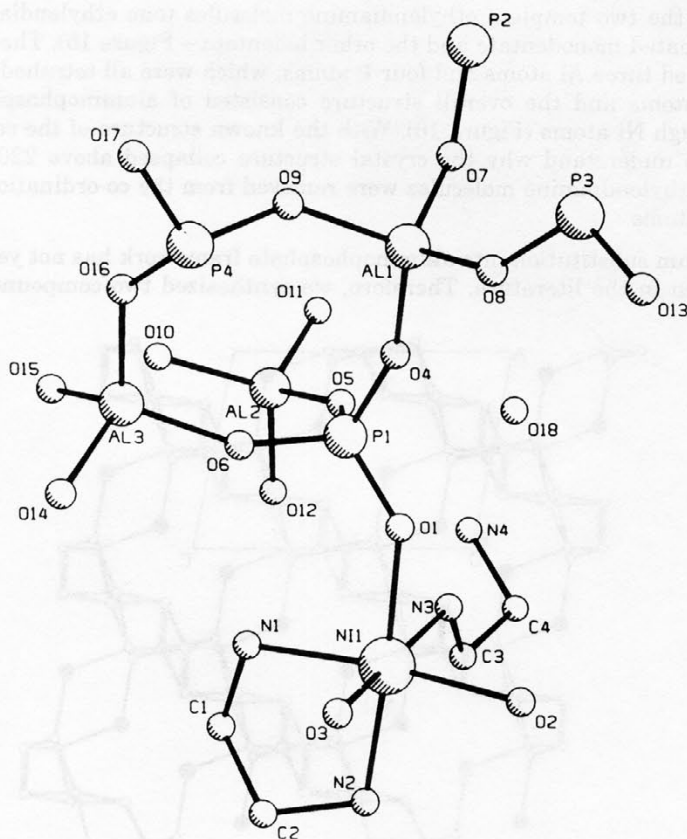


Figure 15. Octahedral environment of the nickel atoms in a new, nickel-containing aluminophosphate. One ethylenediamine molecule is monodentate, and the other bidentate co-ordinated to Ni atoms (reproduced with permission from Ref. 63).

tution of Al^{3+} by Co^{2+} takes place at 4-co-ordinate, tetrahedral site (Figure 14), which is consistent with the blue colour of the crystals. From site occupancy refinement, about 6 atom percent of tetrahedral aluminium is replaced by cobalt.

Our attempts to substitute Al in aluminophosphate framework with Ni resulted in a material for which UV-visible spectroscopy suggested that Ni^{2+} ions replaced hexacoordinated aluminium.⁶² The spectra showed Ni^{2+} ions octahedrally co-ordinated by the O atoms of the aluminophosphate skeleton, and also by H_2O molecules and by N atoms of the ethylenediamine molecules.

The preparation of NiAPO material was analogous to the one previously mentioned for CoAPO-21,⁵⁹ except that the reaction mixture contained nickel acetate instead of cobalt acetate. Initial expectations were that the framework structure would be of the AlPO_4 -21 type, with substitution of octahedral Al atoms by nickel. Determination of the structure showed that a totally novel structure had been formed,⁶³ in which nickel appeared to occupy the octahedral site almost exclusively. The nickel atom is co-ordinated to two framework O atoms, to one water molecule and to three N atoms of the two template ethylenediamine molecules (one ethylenediamine molecule co-ordinated monodentate and the other bidentate – Figure 15). The framework also contained three Al atoms and four P atoms, which were all tetrahedrally bound to oxygen atoms and the overall structure consisted of aluminophosphate layers linked through Ni atoms (Figure 16). With the known structure of the compound, it was easy to understand why the crystal structure collapsed above 220 °C⁶² when water and ethylenediamine molecules were removed from the co-ordination sphere of the nickel atoms.

Chromium substitution into aluminophosphate framework has not yet been definitely proven in the literature. Therefore, we synthesized two compounds with the

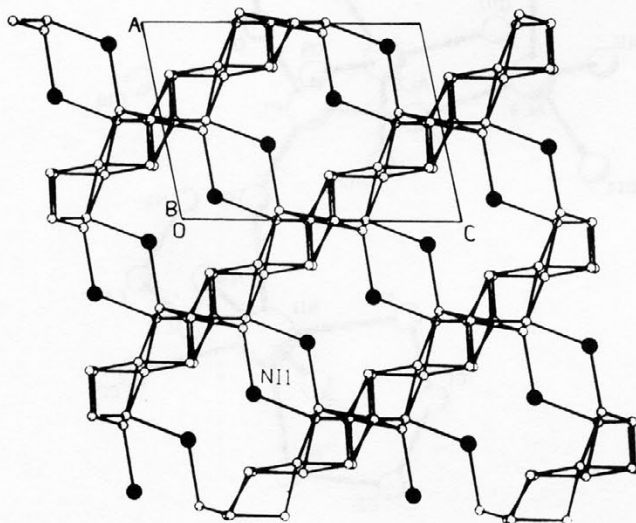


Figure 16. Aluminophosphate layers linked through nickel atoms. There is an octahedral environment around the nickel atom (filled circles), which is not shown because H, O and C atoms have been omitted for clarity (reproduced with permission from Ref. 63).

aim of incorporating chromium into the framework and for CrAPO-14⁶⁴ the X-ray diffraction results show that this has been successfully achieved. In CrAPO-14, all four independent P atoms are tetrahedrally co-ordinated to oxygen while, of the four independent Al atoms, two Al atoms are tetrahedral, one five- and one six-co-ordinated, and the refinement of the site occupancy indicates 4–5% Cr substitution at the six-coordination site. The structure is a close analogue of GaPO-14⁶⁵ with Al replacing Ga. Chemical analysis of a bulk sample and microprobe analysis of three individual crystals also indicated the presence of chromium and, together with the structural data, this is the first definite proof for chromium to substitute aluminium in the aluminophosphate framework.

For SAPO-43 no replacement of Al by Cr to a significant extent could be established.⁶⁴ The structure is like that of gismondine.⁶⁶ It is interesting to note that the crystal of SAPO-43 was relatively small, $0.05 \times 0.03 \times 0.05$ mm³, and that one set of diffraction data was measured by synchrotron radiation. The second set of data was collected on the Rigaku AFC-5R, with a rotating anode source, which was capable of giving good diffraction data for the crystal of so small a volume.

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SAŽETAK

Struktura zeolita i aluminofosfatnih molekulskih sita

V. Kaučič

Zeoliti i druga molekulska sita mikroporozne su kristalne tvari, a glavna im je primjena u katalizi, reakcijama ionske izmjene i kao adsorbensa. Dan je pregled njihovih kristalnih struktura, načina identifikacije kao molekulskih sita, te kratak opis katalitičke aktivnosti. Isto je tako dan prikaz aluminofosfata, te nove, brzo rastuće obitelji mikroporoznih materijala, s posebnim osvrtom na mogućnosti uvođenja različitih metalnih iona u aluminofosfatnu trodimenzijsku strukturu. Kemijske promjene u takovim strukturama dovode do velikog broja strukturnih tipova, a nude i neograničen broj parametara za dizajn aluminofosfatnih materijala s katalitičkim i adsorbirajućim svojstvima. Prikazani su postignuti rezultati sinteze i rentgenske karakterizacije aluminofosfata supstituiranih različitim metalima.