

MOLECULAR SIEVES

PRINCIPLES OF SYNTHESIS AND IDENTIFICATION

R. Szostak

Van Nostrand Reinhold Catalysis Series

MOLECULAR SIEVES

Principles of Synthesis and Identification

R. Szostak

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Preface

“Abracadabra”—a word that has been in use for nearly 2000 years. The early Romans believed that the god Abraxax could help shield a person from evil if the god’s name were inscribed in stone and worn on the person. Individuals new to the zeolite field who have been assigned by their manager or research advisor to prepare a zeolite, and who have experienced the frustrations of attempting to crystallize these materials for the first time, certainly may have thought of using this incantation, followed by the sprinkling of zeolite powder on the laboratory. Unfortunately, despite great strides being made in understanding the fundamentals of zeolite formation, an incantation and the shaking of my old industrial lab apron over all new autoclaves sometimes still appears to be the only way to encourage the crystallization of certain zeolite materials in my laboratory.

Although zeolite synthesis may still seem an art to many, it nonetheless can be understood, appreciated, and successfully performed. This book focuses on the student or scientist who has little experience in the realm of zeolite crystallization. The intent is to provide insight into the fundamentals of zeolite synthesis and the techniques employed to encourage crystal formation. Making a white powder is by no means the end of the road in preparing zeolite materials; it is equally important to be able to identify the materials that have been prepared. Thus one cannot compile a text discussing methods of synthesis without considering the methods employed to characterize the materials prepared. In addition to being a basic text for the synthesis and characterization of zeolite and molecular sieve materials, it is hoped that the compilation of information presented in this book will also serve as a quick reference for those actively working in this field.

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1

Molecular Sieves for Use in Catalysis

STRUCTURAL OVERVIEW

Zeolites and molecular sieves are finding applications in many areas of catalysis, generating intense interest in these materials in industrial and academic laboratories. As catalysts, zeolites exhibit appreciable acid activity with shape-selective features not available in the compositionally equivalent amorphous catalysts. In addition, these materials can act as supports for numerous catalytically active metals. Major advances have occurred in the synthesis of molecular sieve materials since the initial discovery of the synthetic zeolite molecular sieve types A, X, and Y, and a great number of techniques have evolved for identifying and characterizing these materials. Added to an extensive and ever growing list of aluminosilicate zeolites are molecular sieves containing other elemental compositions. These materials differ in their catalytic activity relative to the aluminosilicate zeolites and may have potential in customizing or tailoring the molecular sieve catalyst for specific applications. Elements isoelectronic with Al^{+3} or Si^{+4} have been proposed to substitute into the framework lattice during synthesis. These include B^{+3} , Ga^{+3} , Fe^{+3} , and Cr^{+3} substituting for Al^{+3} , and Ge^{+4} and Ti^{+4} for Si^{+4} . The incorporation of transition elements such as Fe^{+3} for framework Al^{+3} positions modifies the acid activity and, in addition, provides a novel means of obtaining high dispersions of these metals within the constrained pores of industrially interesting catalyst materials.

Another class of materials shown to crystallize into molecular sieve structures are the aluminophosphate (AlPO_4) molecular sieves. Structural analogs to the zeolites as well as new structures have been prepared with this elemental composition, including one with a pore size greater than that of faujasite. Unlike the zeolites, these materials have no ion exchange capacity, as they possess a balanced framework charge. Through modification of synthesis conditions, silicon has been incorporated into many of the AlPO_4 structures. Addition of structural silicon enhances both hydrophilicity and catalytic acid activity, and ion exchange capacity is imparted. Other ions such as magnesium, zinc, cobalt, and manganese also may occupy sites in the AlPO_4 framework. These materials are expected to contain different

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charged sites within the structure, potentially providing further alteration (tailoring) of catalytic behavior.

The possibilities for new zeolite structures and new molecular sieve materials appear limited only by the abilities of those skilled in synthesis to develop methods for their preparation and of the physical scientist to identify and characterize their structure and properties.

MOLECULAR SIEVE VS. ZEOLITE: A DEFINITION

With the recent discoveries of molecular sieve materials containing other elements in addition to, or in lieu of, silicon and aluminum, the casual interchange of the terms “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 (1). He proposed that for a material to be a molecular sieve, it must separate components of a mixture on the basis of molecular size and shape differences. Two classes of molecular sieves were known when McBain put forth his definition: the zeolites and certain microporous charcoals. The list now includes the silicates, the metallosilicates, metalloaluminates, the AlPO_4 's, and silico- and metalloaluminophosphates, as well as the zeolites. The different classes of molecular sieve materials are listed in Figure 1.1. All are molecular sieves, as their regular framework structures will separate components of a mixture on the basis of size and shape. The difference lies not within the structure of these materials, as many are structurally analogous, but in their elemental composition. Therefore, all are molecular sieves though none but the aluminosilicates should carry the classical name, zeolite.

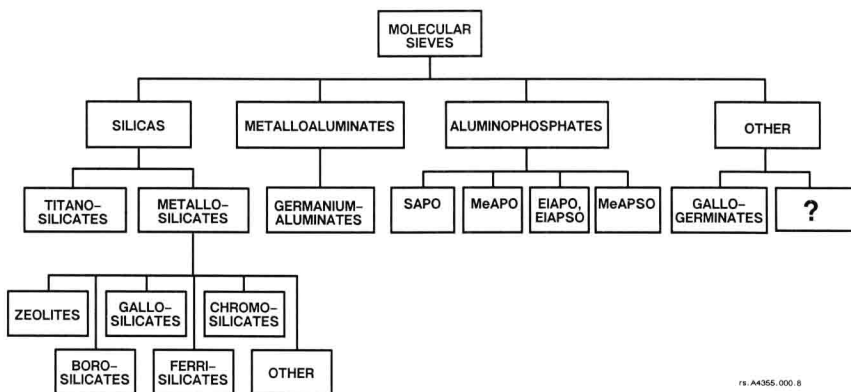
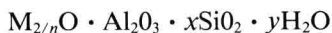


Figure 1.1. Classification of molecular sieve materials indicating the extensive variation in composition. The zeolites occupy a subcategory of the metallosilicates.

Zeolite. Structurally, the zeolite is a crystalline aluminosilicate with a framework based on an extensive three-dimensional network of oxygen ions. Situated within the tetrahedral sites formed by the oxygen can be either a Si^{+4} or an Al^{+3} ion. The AlO_2^- tetrahedra in the structure determine the framework charge. This is balanced by cations that occupy nonframework positions. A representative empirical formula for a zeolite is written as:



M represents the exchangeable cations, generally from the group I or II ions, although other metal, nonmetal, and organic cations may also be used to balance the framework charge, and n represents the cation valence. These cations are present either during synthesis or through post-synthesis ion exchange. The value of x is equal to or greater than 2 because Al^{+3} does not occupy adjacent tetrahedral sites. The crystalline framework structure contains voids and channels of discrete size, unlike the microporous charcoal molecular sieves, a characteristic that separates them from the amorphous carbon molecular sieves. The pore or channel openings range from 3 Å to 8 Å, depending on the structure. Water molecules present are located in these channels and cavities, as are the cations that neutralize the negative charge created by the presence of the AlO_2^- tetrahedra in the structure. Typical cations include: the alkaline (Na^+ , K^+ , Rb^+ , Cs^+) and alkaline earth (Mg^{+2} , Ca^{+2}) cations, NH_4^+ , H_3O^+ (H^+), TMA^+ (tetramethylammonium) and other nitrogen-containing organic cations, and the rare-earth and noble metal ions.

Molecular Sieve. A molecular sieve framework is based on an extensive three-dimensional network of oxygen ions containing generally tetrahedral-type sites. In addition to the Si^{+4} and Al^{+3} that compositionally define the zeolite molecular sieves, other cations also can occupy these sites. These cations need not be isoelectronic with Si^{+4} or Al^{+3} , but must have the ability to occupy framework sites. Cations presently known to occupy these sites within molecular sieve structures are listed in Table 1.1. The zeolite molecu-

Table 1.1. Cations that may form molecular sieve framework structures and the metal oxide charge possible.

M	
$(\text{M}^{+2}\text{O}_2)^{-2}$	Be, Mg, Zn, Co, Fe, Mn
$(\text{M}^{+3}\text{O}_2)^{-1}$	Al, B, Ga, Fe, Cr
$(\text{M}^{+4}\text{O}_2)^0$	Si, Ge, Mn, Ti
$(\text{M}^{+5}\text{O}_2)^{+1}$	P

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lar sieves display a net negative framework charge; however, a molecular sieve framework need not display any charge. Molecular sieves containing only Si^{+4} in the tetrahedral sites will have a neutral framework and exhibit a high degree of hydrophobicity and no ion exchange capacity. The net charge on the AlPO_4 molecular sieves is also zero, arising from framework AlO_2^- and PO_2^+ units existing in equal amounts in these structures. The AlPO_4 's have no ion exchange capacity but exhibit modest attraction toward water due to the polar nature of the Al–O–P moiety within the structure. The possibility of molecular sieves containing sites that are other than tetrahedral in forming their structures will be pursued in Chapter 5.

The conventional name, zeolite, will be used in this text when reference is made to the aluminosilicate molecular sieves. Molecular sieve materials with compositions other than or in addition to silicon and aluminum will collectively be considered under the more general category of molecular sieves. A summary of the distinctions between these designations, zeolite and molecular sieve, is given in Table 1.2.

WHEN IS AN ALUMINOSILICATE NOT A ZEOLITE?

Until recently the zeolite structure was thought to require a high proportion of aluminum for its formation. With the discovery of the high-silica molecular sieves such as zeolite ZSM-5 and silicalite, it was realized that aluminum was not a crucial component in the formation of the microporous structures. In these materials aluminum can be present in as little as trace quantities within a given structure. In very high-silica materials, aluminum inhomogeneity from one unit cell to another could occur. At these low concentrations of framework aluminum it becomes statistically possible to have unit cells that contain no aluminum at all. This raises a question about the limits on defining these high-silica materials as zeolites. Should they be defined only in the broad sense as molecular sieves? In the context of this book, an aluminosilicate will be called a molecular sieve but not a zeolite when there is less than one aluminum ion per unit cell based on the bulk composition of the sample, with no allowance made for inhomogeneities

Table 1.2. Differentiation between the definitions of a molecular sieve and a zeolite for this book.

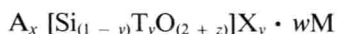
MOLECULAR SIEVE	ZEOLITE
Microporous crystalline structure	Microporous crystalline structure
Variable elemental composition	Aluminosilicate
Variable framework charge	Anionic framework

within the individual crystal on the microscopic level. Haag et al. (2) have calculated occupancy of aluminum within a unit cell for the high-silica form of zeolite ZSM-5, which has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 190. This is equivalent to one aluminum per unit cell. If random aluminum distribution occurs among all the sites, 36% of all unit cells have no aluminum, whereas the others have one, two, three, or more aluminum ions. For a silica/alumina ratio of 96, which is an average of two aluminum ions per unit cell, 14% of the cells would still contain no aluminum ions. It is true that defining the chemical composition for high-silica aluminosilicates based on bulk composition appears to hold little meaning at the individual unit cell level. On the other hand, applicability of these materials as catalysts and adsorbents generally relies on their bulk or average properties. Therefore these aluminosilicates will be considered zeolites if they have at least, on the average, one aluminum per unit cell. The aluminosilicate with the ZSM-5 structure, for example, will be considered a zeolite at silica/alumina less than 190. Materials of this structure with silica/alumina above 190 will be considered only as molecular sieves. Silicalite-1 or silicalite, is a name proposed by Flanigen et al. (3,4) to identify the pure silica polymorph of zeolite ZSM-5(147). In the appendix an exception is made: the X-ray diffraction patterns for the high silica/aluminum-free silica molecular sieves are listed under zeolites because many of these materials have claims of higher aluminum content in the patents. (Also this is done to limit the number of categories included there for brevity.)

The same convention will be used for zeolites containing trace amounts of other elements in the framework ion positions. For example, a molecular sieve material containing both aluminum and iron in a silicate matrix will be considered a zeolite if the number of iron ions averages less than one per unit cell. At greater than one iron per unit cell, the material will be referred to as an aluminoferrisilicate molecular sieve. The position of the aluminum relative to iron in the term "aluminoferrisilicate" is based simply on an alphabetical ordering of the elements. An example of an aluminoferrisilicate zeolite is the natural zeolites. Historically, the natural zeolites were known to contain trace amounts of iron within their framework. With the high percentages of framework aluminum and the low quantity of framework iron in these materials, they would retain their classification as zeolites, and should then be considered zeolites containing framework impurities of iron. The definitions presented here are consistent with those definitions proposed by Smith (5) and Breck (6). According to those authors, zeolites are aluminosilicate structures that possess exchangeable cations and reversibly adsorb and desorb water. According to the Smith and Breck definitions, silica analogs and the metasilicates, as well as the aluminophosphates, silicoaluminophosphates, and metalloaluminophos-

phates, are molecular sieves and not classic zeolites, based on their chemical composition and framework charge.

This, however, is not the only set of definitions in use to date. Liebau defines a zeolite as a tectosilicate that contains "tunnels or larger polyhedral cavities interconnected by windows large enough to allow ready diffusion of the polyatomic guest species through the crystal" (7). Broadly defined in this manner, a zeolite would encompass not only the well-known aluminosilicates but the pure silica polymorphs and the metasilicates, as well as the phosphate-containing molecular sieves. A general formula put forth under Liebau's definition would be:



where A, X, and M are nonframework cations (A), anions (X), and neutral species (M). T is an atom that structurally replaces the silicon ions. This basis of the definition of the zeolite is as a substituted silica, and the formula collapses to the pure silica molecular sieve when $x = y = z = v = 0$. This is in line with Rees's philosophical argument: "When is a zeolite not a zeolite but a defect silica?" (8). This point is raised in the discussion of aluminosilicates that can crystallize under a wide range of silica/alumina (20 to ∞), where at high silica/alumina ratios these materials contain on the average less than one aluminum ion per unit cell. Here, an inhomogeneity of the number of aluminum ions per unit cell might well be considered to produce a defective form of crystalline silica. It is thought that the use of the tectosilicate as the basis for defining a zeolite or molecular sieve may be too restrictive in light of the newer, nonsilicate based materials now being reported. Thus the distinction used in this book between the zeolite and the molecular sieve will be that summarized in Table 1.2.

LOEWENSTEIN'S RULE

Loewenstein has formulated certain rules that may govern the linking together of silica tetrahedra and of the tetrahedra and octahedra of alumina (9). The distribution of tetrahedra in a crystal is not entirely random in amorphous and crystalline aluminosilicates.

(1) Whenever two tetrahedra are linked by one oxygen bridge, the center of only one of them can be occupied by aluminum; the other center must be occupied by silicon or by another small ion of electrovalence 4 or more, such as phosphorous.

(2) Whenever two aluminum ions are neighbors to the same oxygen anion, at least one of them must have a coordination number larger than 4, that is, 5 or 6, toward oxygen.

These rules explain the maximum substitution of 50 percent of the silicon in three-dimensional framework networks of tetrahedra by aluminum. For 50 percent substitution, rigorous alternation between silicon and aluminum tetrahedra becomes necessary. To date no deviation from these rules has been observed in the zeolite systems, the aluminophosphates, or the metallosilicates studied. The validity of these rules for the other molecular sieve systems will be discussed further in Chapter 4.

PORES AND CHANNELS: FROM SIMPLE TO COMPLEX

Numerous attempts have been made to group or classify zeolites on the basis of different structural elements. The kind of building unit most suitable for the classification of the zeolites depends on the property under consideration. Where interest in a particular zeolite is based on its ability to selectively adsorb one component of a mixture over another, a detailed understanding of the way the polyhedra stack within the zeolite structure is not necessary. It is, however, important to identify the size of the pore opening necessary to achieve the desired selectivity. For example, zeolite types A and X differ in their adsorption properties for organic molecules. In a process that requires the separation of linear from branched paraffins, calcium exchanged zeolite type A would be the preferred zeolite. The size of the pore opening of this zeolite (4.8 Å) results in selective adsorption of the small unbranched hydrocarbons by this zeolite. The branched hydrocarbons are too large to readily enter the pores of this structure. Type X with its large pore channel system (7.6 Å) would not be selective in such a process, as it will adsorb both the linear and the branched hydrocarbons. Thus, on the basis of their selectivity properties alone, we can classify these zeolites without necessarily knowing the details of the structures of either material. A difficulty in classifying zeolites is the lack of detailed structural information. Only a handful of zeolites synthesized to date have had their structures completely determined. But the lack of structural data does not restrict the determination and utilization of the pore size of these materials. Numerous applications of these zeolites have been explored and catalytic processes developed without prior knowledge as to the exact three-dimensional spatial arrangement of the ions within the framework structure.

On the other hand, in trying to understand the relationship between different structures, a more detailed description, using a specific set of structural building units, becomes necessary. Two zeolites, offretite and erionite, are well-known examples of structures that tend to coexist both naturally and under certain hydrothermal crystallization conditions. These structures differ from one another according to the stacking sequences of their puckered sheets. With slight changes in the stacking sequence of offretite, the