MOLECULAR SIEVES PRINCIPLES OF SYNTHESIS & IDENTIFICATION

Molecular Sieves
Principles of Synthesis and Identification

Second Edition

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Molecular Sieves

Dedication

To Dr Edith M. Flanigen, the late Dr Tudor L. Thomas and the late Professor Lenard B. Sand, three people who have had a positive influence on my career in the field of zeolites and molecular sieves.

Preface to the second edition

> 'Where are you going?' said the woman.
> 'To prove what a great hunter I am, I'm going out to hunt me a bear', replied the man with the gun.
> 'Are you sure you can find a bear?' said the woman.
> 'I'm going out to hunt a bear and dang it, I will find me a bear', replied the hunter.
> He went out to find himself a bear and came home with a possum.
>
> *Obscure southern American folk tale*

Since the publication of the first edition of this book, an explosion of new materials and novel structures has occurred in the field of zeolites and molecular sieves. Nine molecular sieve materials have found industrial application. These include the zeolites MAP(GIS), L(LTL), beta(BEA), and ferrierite(FER); the high silica phases, theta-1(TON) and MCM-22(MWW); the titanium silicate, TS-1; and the aluminophosphate-based materials, SAPO-11(AEL) and SAPO-34(CHA). We are now into the third and fourth generation of materials, many bearing little resemblance to the zeolites found in nature. The initiator for the explosion has been the forward thinking of the many scientists around the world who reached beyond the known aluminosilicate compositions to potter about in other parts of the periodic table. It must not be forgotten that these discoveries were built upon a strong previously developed methodology. The cause–effect knowledge of the various parameters of zeolite synthesis, the role of cations, mineralizing agents, the addition of organic additives and an understanding of the oxide chemistry of amphoteric elements have all helped to shape the development of these new materials. This book is not meant to be an exhaustive review of zeolite synthesis. There are numerous other publications which provide updates in various aspects of research in the zeolite field. The primary focus of this book is to provide background in the understanding of the methodology of zeolite and molecular sieve synthesis by examining the approaches taken to develop new materials and methods used to characterize them.

How do these uniquely beautiful structures form? This is a question that has enticed many to propose and study the mechanisms of zeolite nucleation and crystal growth. The aspects of nucleation and crystal growth are as basic as a Georgia possum. But like the hunter in the fable, many have set out to search for something exotic to explain how these porous materials come to be. Those who have been deeply involved in the laboratory synthesis of zeolite and molecular sieve phases appreciate the complexity of the subject. Great strides have been made by several research groups in the last few years, in successfully bridging the gap between the general formation mechanisms of crystalline phases and the precipitation of complex structures known as the zeolites. The application of these basic crystal growth principles to the formation of zeolite phases has led to significant advancements in the development of zeolite membranes and thin films. The essence of what is involved in nucleation and crystal growth as it relates to zeolite synthesis is presented in this book.

But what is a zeolite? The introductory chapter of this book provides an historical summary of the struggle to come up with an easily memorable naming system, and later to differentiate the natural zeolites from the microporous materials made up of vastly different compositions. To date, there is no satisfactory standard set of nomenclature developed for either. But it is hoped that the utilization of the structure code in conjunction with the common name of the phase being discussed in this edition will help those who are not intimately familiar with the innumerable names used to describe materials which are topologically related.

It is my sincere hope that the readers and students utilizing this edition will acquire a good sense of the history of zeolite synthesis. The methodology developed by the many talented scientists who have entered this field before them should provide them with the tools needed to prepare microporous phases. The successes of past discoveries should inspire them to continue the quest for potentially useful new phases.

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1 Molecular sieves: history and nomenclature

> The scientist and engineer are always seeking new materials with properties which permit improvements of old processes or developments of new ones. The molecular sieves are just such materials, and with hindsight one wonders why it took so long for their potentialities to be realized.
>
> *R.M. Barrer, from the General Introduction notes for the 1st International Zeolite Conference, London, 1968*

1.1 Molecular sieves today

A group of minerals that was once a curiosity of the geologist has today turned into a high-value commercial family of materials. Zeolites are playing an ever increasing role in an era of environmental awareness and regulation. There are three properties of the zeolite molecular sieves that make them commercially viable: they are selective and strong adsorbers, they are selective ion exchangers and, when the cation is a proton, they are superb solid acid catalysts. As catalysts their environmental advantages include decreased corrosion, improved handling, decreased toxic effluent and minimal undesirable by-products.

Today, zeolites impact a diverse range of industries. Nearly every step in the refining of petroleum now involves the use of a zeolite as a catalyst, catalyst support or adsorbent. In addition to petroleum applications, these materials are found in a range of adsorption applications from catfish farms to cat litter boxes. Several zeolites are effective in removing ammonia and disagreeable smells from the environment. The cold winters in northern countries are made less extreme through the use of double-pane windows which keep the chill out and the heat in. A strip of zeolite containing material between the panes of glass adsorbs the excess humidity preventing fogging of the windows, so that the building inhabitants can have an unfrosted view of the landscape. As ion exchangers, zeolites have a high specificity towards certain ions, and will take the radioactive counterparts out of the effluent of a nuclear power plant. Due to phosphate restrictions in many parts of the world, zeolites are acceptable detergent builders due to their attraction for calcium and magnesium ions which constitute the 'hard' in hard water. By far, the use of zeolites in laundry products represents the largest non-reusable bulk application for this kind of material [1, 2].

Major advances have occurred in the synthesis of molecular sieve materials since the initial discovery of the synthetic zeolite molecular sieve types A(LTA), X(FAU) and Y(FAU), 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 crystalline molecular sieves containing other elemental compositions. These materials differ in their catalytic activity relative to the aluminosilicate zeolites and have found their potential in further customizing or tailoring molecular sieves for specific applications. Due to their many common features, discussions of zeolites generally include discussion of these other microporous crystalline phases. Most closely associated with the zeolites are materials containing elements isoelectronic with Al^{3+} or Si^{4+}, as they can form metal silicates with zeolite-like structures. These include the tetravalent Si^{4+}, the trivalent B^{3+}, Ga^{3+} and Fe^{3+}, and divalent Zn^{2+} and Be^{2+} substituting for Al^{3+}, and Ge^{4+} and Ti^{4+} for Si^{4+}. The incorporation of transition elements modifies the catalytic activity and, in addition, provides a novel means of obtaining high dispersions of these metals within the constrained pores [3–5].

A more recent class of microporous materials shown to form zeolite-like structures are the aluminophosphate ($AlPO_4$) molecular sieves [6]. Structural analogs to the zeolites as well as new structures have been prepared with this elemental composition, including several with pore sizes greater than that of known zeolites. These materials have no ion exchange capacity as they possess a balanced framework charge. What differentiates these materials from the zeolites is that many contain framework aluminum in coordination other than the classic tetrahedral coordination of aluminum found in the zeolites. The ability of the aluminophosphates to have mixed coordination of aluminum in the structure increases the diversity of structures beyond what is possible in the aluminosilicates. 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 as 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 framework charge sites and different framework catalytic activity, potentially providing a unique method of altering (tailoring) the properties to specific applications.

Today, it is well established that a variety of elements can form open oxide structures with characteristics similar but not always identical to the zeolites; thus the possibilities for new structures and new crystalline microporous molecular sieve materials appear to be limited only by the abilities of those skilled in synthesis to develop methods for their preparation, and of the analytical scientist to identify and characterize their structure and properties.

1.2 Zeolithos

The name 'zeolite' is said to have its origin in the two Greek words *zeo* and *lithos*, which mean 'to boil' and 'a stone' [7, 8]. The phenomena of melting and boiling at the same time is termed **intumescence**. The name 'zeolite' was first used by the Swedish mineralogist Cronstedt to describe stilbite(STI), the first mineral zeolite identified. It was discovered in 1756. It took another 100 years before the reversible desorption/adsorption of water in this mineral was documented [9]. However, within a few years of this discovery the ion exchange properties were noted [10]. Though the ability to adsorb organic and various small molecules was first recorded around the turn of the 20th century [11], the shape-selective nature was first noted in 1925. It was not until 1932 that the term 'molecular sieve' was established by McBain and applied to the zeolite minerals [12]. Although the properties of the zeolites were becoming more well defined, it was not until the advent of X-ray crystallography for structure determination in the late 1920s that the first solid information about framework topologies of these unique minerals began to unfold [13–15]. It is interesting to note that even today it is common to have a detailed understanding of the adsorptive and catalytic properties of a new zeolite long before the exact structural details of the material are known. (It should be noted that in 1816 the mineral allophanes were suggested by Hausmann and Stroymeyer to also be included in the newly defined zeolite group an early indication of the looseness by which this mineral family was later to be defined. (F. Stromeyer, J.F.L. Hausmann, *Gottingische Gelehrte Anzeigen*, **2**, 1249 (1816) translated by Dr. Gottlieb-G. Lindner).)

1.3 Early commercial zeolites

Zeolites were first commercialized in 1954 [16–18]. These commercial zeolites were not the natural zeolite minerals which had formed the basis of the early studies, but new synthetic materials developed at the Tonawanda (NY, USA) research laboratories of Linde. These first zeolites, identified simply as (types) A(LTA), X(FAU) and Y(FAU) still represent the most important of the commercial zeolites in use today and were identified commercially as Linde Molecular Sieves (LMS). The first applications of zeolites were in refrigerant desiccants and in the drying and sweetening of natural gas, both applications utilizing the 'water-loving' or **hydrophilic** nature of the zeolite. The first use of the 'molecular sieve' nature of the material occurred in 1959 with the ISOSIV process [19]. This process separated linear hydrocarbons from the branched members. Other industries rapidly became interested and involved in the zeolite field. In the late 1950s Davison Chemical (now of W.R. Grace and Co.) produced zeolites under the trade name 'Microtraps'. It was Mobil Oil that introduced the use of zeolite X(FAU) as a refinery cracking catalyst in